THE JOURNAL

OF THE

American Chemical Society

VOL. LIV

MAY—AUGUST

1932

Editor

ARTHUR B. LAMB

Associate Editors

ROGER ADAMS
J. R. BAILEY
WALLACE H. CAROTHERS
H. T. CLARKE
R. A. GORTNER
J. H. HILDEBRAND
ARTHUR E. HILL
FRANK B. KENRICK
E. P. KOHLER
G. E. F. LUNDELL
JAMES W. MCBAIN
W. A. NOYES
HUGH S. TAYLOR
E. W. WASHBURN

EASTON, PA.
MACK PRINTING COMPANY
1932

The Journal of the American Chemical Society

VOL. 54 MAY, 1932 No. 5

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

THE DECOMPOSITION OF DIAZOBENZENE CHLORIDE IN WATER SOLUTION[1]

BY CECIL J. HAGGERTY AND BARTHOLDT C. HADLER

RECEIVED SEPTEMBER 5, 1931 PUBLISHED MAY 7, 1932

Introduction

The kinetics of the decomposition of the diazo bodies in water solution have been studied rather extensively by various investigators, *viz.*, Hausser and Muller,[2] Hantzsch[3] and Cain and Nicoll.[4]

More recently Pray,[5] Yamamoto[6] and Blumberger[7] have continued investigations on these same decompositions. An examination of the data of these various individuals will show that the addition of those substances which hydrolyze alkaline give larger velocity constants but that there is a diminished evolution of nitrogen. This is claimed to be due to the so-called coupling reactions which are supposed to take place in the presence of hydroxyl ion in preference to the simple decomposition. Blumberger states that there is a maximum in the curve of reaction rate plotted against hydroxyl ion increase.

It is the purpose of the present paper to show that the decreased evolution of nitrogen is not due to the so-called coupling reactions and that the maximum in the curve of reaction rate against hydroxyl ion is not attributable simply to this ion.

Materials and Apparatus.—Ordinary aniline was redistilled several times; only that portion which boiled constantly at 183.5° was taken for the subsequent experiments. The other chemicals were of C. P. grade and no further attempts at purification were made.

---

[1] This paper is constructed from a thesis submitted by Bartholdt C. Hadler to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Hausser and Muller, *Bull. soc. chim.*, [3] **7**, 721 (1892); *Compt. rend.*, **114**, 549, 669, 760, 1438; *Bull. soc. chim.*, [9] 353 (1893).

[3] Hantzsch, *Ber.*, **33**, 2517 *ff.* (1900).

[4] Cain and Nicoll, *J. Chem. Soc.*, **81**, 1412 (1901); **83**, 206, 470 (1903); *Ber.*, **38**, 2511 (1905).

[5] Pray, *J. Phys. Chem.*, **30**, 1417, 1477 (1926).

[6] Yamamoto, *J. Soc. Chem. Ind. Japan*, **32**, 352 (1929).

[7] Blumberger, *Rec. trav. chim.*, **49**, 276 (1930).

The reaction vessel consisted of a large test-tube about 15 cm. long and 2.5 cm. in diameter to which had been sealed a capillary side arm. The latter communicated with the water-jacketed gas-measuring buret which was maintained at the same temperature as the thermostat by circulating water from the latter through the former. The aniline hydrochloride was diazotized below 5° and upon completion of this process the solution was placed in the reaction vessel. After adding that substance whose effect we wished to investigate, a mercury-sealed stirrer was fitted into place and rotated at a constant speed. The gas-measuring buret could be adjusted and read accurately to within 0.1 cc., which, in the early stages of the reaction, leads to an error of 3 or 4%. All of the experiments were conducted at 30 ± 0.01°. The volume of nitrogen evolved was recorded at thirty-minute intervals. These gas volumes were reduced to standard conditions and the reaction velocity constants were calculated according to the graphical method of Guggenheim,[8] which is supposed to overcome uncertainties in the value of A in the ordinary unimolecular equation.

Experimental

The following experiment is selected as being typical of this decomposition. In this table, as in all following tables, the first column contains the time in minutes; the second column, the corrected amount of nitrogen evolved; the third column, the value of $v-v_0$; the fourth column, the $\log_{10}$ of $v-v_0$; the fifth column, the same value as read from the graph; and the last column gives the value of $0.4343\ K \times 10^4$.

TABLE I

EXPERIMENTAL RESULTS

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343\ K \times 10^4$
30	4.0	4.0	0.602	0.607	
60	7.3	3.3	.519	.536	
90	10.4	3.1	.491	.465	
120	13.1	2.7	.431	.393	23.8
150	15.3	2.2	.342	.323	
180	17.0	1.7	.230	.250	
210	18.4	1.4	.146	.178	

The value 23.8 was obtained from the straight-line plot of $\log_{10} v-v_0$ against the time. This value agrees very well with the value 24.0 as found by Pray for this same decomposition.[9]

It has been stated by Pray and others that any substance which exerts a dehydrating effect will retard the velocity of decomposition. He observed this in his study of the effect of sulfuric acid on this decomposition. We give in the following table the effect of sulfuric acid on this decomposition mainly because we will need the constant for subsequent discussion. The sulfuric acid was added to the diazotized aniline hydrochloride in the molar ratio of fifteen to one.

The tabulated data show definitely that there is a decrease in the reaction velocity constant in the presence of sulfuric acid. Blumberger attributes

[8] Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[9] Pray, Ref. 5, p. 1481.

TABLE II

RESULTS IN PRESENCE OF SULFURIC ACID

Time	Nitrogen evolved	$v-v_0$	log $v-v_0$	Calcd.	0.4343 $K \times 10^4$
60	6.6	6.6			
90	9.6	3.0	0.477	0.477	
120	12.1	2.5	.398	.417	
150	14.4	2.3	.362	.357	
180	16.3	1.9	.279	.296	20.1
210	18.1	1.8	.255	.235	
240	19.5	1.4	.146	.175	
270	20.8	1.3	.114	.115	

this decrease to the formation of a $C_6H_5N_2SO_4$ ion. If this is true it seems strange that Pray did not observe the decrease on the addition of potassium sulfate. We cannot, therefore, attribute this decrease simply to the formation of a sulfate ion, and it appears that the dehydrating effect is the proper cause of the decrease.

It is known that the diazonium salt is amphoteric. Consequently there is an equilibrium relation as follows

$$C_6H_5N_2^+ + 2OH^- = C_6H_5N_2O^- + H_2O$$

Also large quantities of the $C_6H_5N_2O$ ion cannot exist in the presence of sodium or potassium ion, for the solubility product is exceeded and precipitation takes place. We should expect, therefore, that if certain salts which hydrolyze alkaline or if alkalies are added to the diazo compound, this precipitate of diazotate will follow with a consequent effect on the decomposition rate of the diazo body. Varying amounts of salts or alkalies added will have differing effects according to the above equilibrium. On the other hand, acid or neutral salts should not affect the reaction rate. This can easily be seen by an examination of the data of Pray.

In the following table we give the effect of monosodium dihydrogen phosphate. Since this substance hydrolyzes acidic, we would not, according to the above argument, expect any effect on the reaction rate. The data show this to be the case.

TABLE III

RESULTS WITH MONOSODIUM PHOSPHATE

Time	Nitrogen evolved	$v-v_0$	log $v-v_0$	Calcd.	0.4343 $K \times 10^4$
30	3.5	3.5			
60	7.1	3.6	0.556	0.560	
90	10.3	3.2	.505	.492	
120	13.0	2.7	.431	.420	
150	15.2	2.2	.342	.351	23.3
180	17.2	2.0	.301	.279	
210	18.7	1.5	.176	.210	
240	20.1	1.4	.146	.140	

A comparison of this table with Table I will show an almost exact similarity in the amounts of nitrogen liberated at the various points of time. Of necessity then the constants agree with one another very well. Therefore, in spite of the fact that the molar ratio of salt added to the diazo salt is in this case nine to one, there appears no effect on the decomposition rate.

Although secondary sodium phosphate hydrolyzes faintly basic, yet in sufficient quantity (in this case, nine moles of phosphate to one of diazo compound) the P_H of the diazo solution can be changed enough to cause an apparent increase in the reaction rate, as the following table shows.

TABLE IV

RESULTS WITH SECONDARY SODIUM PHOSPHATE

Time	Nitrogen evolved	$v-v_0$	log $v-v_0$	Calcd.	0.4343 $K \times 10^4$
30	3.8	3.8	0.580	0.575	
60	6.1	2.3	.362	.397	
90	7.9	1.8	.255	.219	59.9
120	9.0	1.1	.041	.040	

The amount of nitrogen liberated in this experiment after a lapse of twenty-four hours was less than half of that obtained in the simple decomposition. This confirms Pray's observation but we do not believe it to be due to the so-called coupling reactions. When the phosphate is added to the diazo solution, a brown precipitate appears. This occurs immediately, and so cannot be attributed to the formation of hydroxyazobenzene, for at the beginning of the reaction there is no phenol present with which the diazo compound might combine. Such behavior is explained according to the previous argument.

Concerning the increase in the reaction rate, for which no one has offered an adequate explanation, may we propose that it is a heterogeneous reaction and so catalyzed by the precipitate of the diazotate. We believe this to be so, for one of us has carried out preliminary experiments on this decomposition in the presence of silica gel and suchar and has found the rate to be approximately tripled in the presence of these substances. These experiments are now in the process of completion and we expect to report them in the future.

The addition of hydrogen ion, according to the above-mentioned equilibrium, should cause a shift to the left and a consequent dissolution of the precipitated diazotate. Normal decomposition would be expected to ensue. This is found to be the case, as the following experiments show. Sodium succinate was added to the diazo solution in the molar ratio of nine to one. Precipitation occurred as with the phosphate. We followed the decomposition of this heterogeneous system for two hours and then added sufficient sulfuric acid to redissolve the precipitate.

TABLE V

RESULTS WITH SODIUM SUCCINATE

Time	Nitrogen evolved	$v-v_0$	log $v-v_0$	Calcd.	0.4343 $K \times 10$
30	1.3	1.3	0.114		
60	2.7	1.4	.146		
90	3.9	1.2	.079		
120	5.2	1.3	.114		
30	2.5	2.5	.398	0.416	
60	4.9	2.4	.380	.356	
90	6.9	2.0	.301	.296	20.1
120	8.6	1.7	.230	.237	
150	10.1	1.5	.176	.176	
180	11.4	1.3	.114	.114	

The first part of this table shows again decreased nitrogen evolution. The rate appears to be constant within experimental error. The second part of the table shows definitely that the precipitated diazotate will go back into solution and decompose in regular fashion. The constant for this portion of the table is exactly the same as that of Table II.

In the following experiment we added sodium hydroxide in the molar ratio of forty to one in an attempt to reduce the decomposition of the diazo solution to a minimum. After one and one-half hours we added sufficient sulfuric acid to redissolve the precipitate.

TABLE VI

RESULTS OF EXPERIMENT

Time	Nitrogen evolved	$v-v_0$	log $v-v_0$	Calcd.	0.4343 $K \times 10^4$
90	0.8				
30	5.4	5.4	0.732	0.725	
60	8.4	3.0	.477	.625	
90	11.5	3.1	.491	.521	33.6
120	13.3	2.8	.447	.421	

It will be observed in this experiment that the sodium diazotate decomposes at a very slow rate, for after ninety minutes' time we obtained only 0.8 cc. The constant obtained from these data shows that the reaction is proceeding at a faster rate than the decomposition in Table II. This is due very likely to the large amount of nitrogen liberated in the early stages of the reaction on account of the heat evolved in the neutralization of the alkali. These data show again that the precipitated diazotate can be redissolved and that the resulting decomposition is in order with the simple decomposition.

As a final test the following experiment was performed. In order to overcome the heat effect of the previous experiment, we prepared some solid sodium diazotate by adding sodium hydroxide to the diazo compound around zero degrees. This we filtered off and washed with cold water until it was free from sodium hydroxide. We dried this in a vacuum

desiccator over sulfuric acid. Thirty-two grams of this dried diazotate was suspended in 20 cc. of distilled water and placed in the reaction vessel. We noted the decomposition of this heterogeneous mixture and after two hours' time sufficient dilute hydrochloric acid was added to cause solution.

TABLE VII

EXPERIMENTAL RESULTS

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343\ K \times 10^4$
120	1.9	1.9			
60	10.4	10.4			
90	14.9	4.5	0.653	0.673	
120	18.9	4.0	.602	.578	30.1
150	21.7	2.8	.447	.487	
180	24.4	2.7	.431	.396	

The constant of this experiment is in fair agreement with those of Tables I and III, and the data again show that the diazotate which is precipitated in alkaline solution can be redissolved, forming the diazo salt which decomposes normally.

What the decomposing entity is we do not know. The facts at hand will not admit of any ion as the deciding factor. We do know, however, that in the simple decomposition hydrogen ion is formed. This being so, the equilibrium above will shift to the left as the reaction proceeds, or, what amounts to the same thing, the amount of substance undergoing decomposition in solution is increased. Under these conditions the value of A in the simple unimolecular equation is not known accurately and if sufficient time is allowed to elapse all of the diazo compound would be expected to decompose. The arbitrary method of selecting say twenty-four hours or of taking readings until an apparently constant value occurs cannot give the correct value of A in the presence of alkalies or of substances which hydrolyze alkaline. Consequently the real reaction rates, under these circumstances, can be obtained only by some method which eliminates such an uncertain value. This has been accomplished in the present paper by selecting the method of Guggenheim.

Summary

1. The simple decomposition of diazobenzene has been repeated.

2. The decomposition in the presence of sulfuric acid shows that the rate is decreased. This is not due, however, simply to the formation of a diazosulfate ion.

3. The decomposition has also been studied in the presence of alkali and of substances which hydrolyze alkaline.

4. It has been shown that if the P_H of the solution is in the neighborhood of 7 or greater, a precipitate will form. This precipitate is an alkali diazotate.

5. This precipitate can be redissolved upon the addition of acids and the resulting diazo compound will follow the normal decomposition.

6. The solid diazotate has been prepared and its decomposition noted. The addition of acid to this solid causes it to redissolve and decompose normally.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ABSORPTION SPECTRA IN SOLUTION AT LOW TEMPERATURES

BY L. B. ARNOLD, JR., AND G. B. KISTIAKOWSKY

RECEIVED OCTOBER 5, 1931 PUBLISHED MAY 7, 1932

Introduction

Extended and systematic work on light absorption of carbon compounds in solution has been concerned mainly with the identification and quantitative study of rather broad absorption regions. Each of these can be assigned to a definite electronic transition in the molecule, at least in cases where information on the absorption spectra in the gaseous state is available. The main achievement of this work is the evidence that certain absorption regions, located mostly in the near and middle ultraviolet, can be identified with definite atomic groups like the carbonyl, double bond, benzene ring, etc. Evidence has also been accumulated indicating that, if more than one such light absorbing group is present in a large molecule, the resulting spectrum can be represented in the first approximation as a sum of the component spectra. A more detailed study, by the usual method of quantitative measurement of the light absorption coefficients, has revealed, however, that the summation rule holds only very approximately and that in general the rest of the molecule exerts an influence on the absorption by a given part of it. Such an effect, as has been pointed out frequently, is altogether analogous to the alterations in the chemical properties of a group produced by the rest of the molecule, that are so common in organic chemistry.

The study of the spectral changes in solution is thus of considerable interest, at least in the domain of large and complicated molecules where neither the Raman spectra nor the absorption spectra in the vapor phase are sufficiently simple to offer a promise of a more rapid and direct solution of the problem. An attempt at a closer theoretical treatment of the absorption coefficient data for homologous molecules is complicated, however, by the circumstance that this experimental method records simultaneously the effects of two essentially different phenomena. In addition to alterations in the energy of electronic levels as well as to more or less mechanical changes in vibrational frequencies of an atomic group, resulting in a shift and modification of bands comprising an absorption

region, the light absorption coefficients are affected by changes in electronic transition probabilities. This latter phenomenon is much less accessible to theoretical treatment and so long as the effects of the two are not separated, an uncertainty is attached to speculations based on the study of the absorption coefficients describing only the large scale structure of absorption spectra. The difficulty is removed, in principle at least, by a study, not of the intensity of absorption, but of the locations of the vibrational bands within the absorption region due to the atomic group investigated and their alterations produced by changes in the structure of the rest of the molecule. The scarcity of work in this direction is due undoubtedly to the diffuseness and frequently to the complete absence of any finer structure in the absorption spectra of organic molecules in solution.

The existing literature indicates that the presence or absence of finer structure is typical of large cl es of organic compounds and is not "accidental."

Hartley[1] has already pointed out that only aromatic hydrocarbons possess finer structure in their spectra, while aliphatic compounds show only continuous absorption. Stark[2] denied this conclusion and showed that some aliphatic hydrocarbons had banded spectra. However, the bands which he finds are of an altogether different appearance from those of aromatic hydrocarbons and comprise, judging from their width, many vibrational transitions, each probably representing a definite electronic level. Thus, on the whole, Stark's objections do not disprove the conclusion of Hartley, but show that it needs modification. The present contribution is concerned with this modification and amplification; it also deals with the problem of the mutual influence of two parts of a molecule as a function of their distance apart.

In an attempt to improve experimental conditions use was made of the old and well-known observation that low temperatures tend to sharpen and bring out the finer details in the spectra of solids and liquids.[3] Further improvement was expected and obtained by the use of an inert and nonpolar solvent, since the influence of the latter on the spectra of solutes is known to be considerable in some cases.[4]

Experimental Details

The experimental set-up consisted of a quartz hydrogen discharge[5] (E, Fig. 1) as a source of continuous ultraviolet light, a Dewar flask with quartz windows and a small

[1] Hartley and Dobbie, *J. Chem. Soc.*, **77**, 846 (1900); **39**, 153 (1881).

[2] Stark and Lipp, *Z. physik. Chem.*, **86**, 43 (1913).

[3] For recent work see particularly Kronenberger, *Z. Physik*, **63**, 494 (1930); Conant and Crawford, *Proc. Nat. Acad. Sci.*, **16**, 552 (1930).

[4] Klingstedt, *Compt. rend.*, **176**, 1550 (1923).

[5] Kistiakowsky, *J. Opt. Soc. Am.*, **2**, 549 (1931).

Hilger quartz spectrograph (F). The construction of the flask will be seen from Fig. 1. (A) are four quartz to Pyrex graded seals, (B) are polished quartz windows sealed to the ends of these and (C) is the absorption cell of quartz, 4 cm. long, placed in line with the windows. Cooling was accomplished by means of liquid nitrogen, whose level was kept somewhat below the absorption cell. A small electric heater (D) placed in the bottom of the flask generated a steady stream of dry nitrogen which kept the absorption cell cool and prevented frost from forming on it and on the inner windows. Exposures were made on Hammer Special plates sensitized with vaseline. The wave length determinations were made by comparison with the copper arc spectrum. Solutions were made by dissolving a weighed amount of the substance in pentane, transparent within the limits of the set-up, and introducing a small known amount of this solution into liquid propane. This procedure was adopted because solutions in the pentane showed a strong tendency to freeze on cooling.

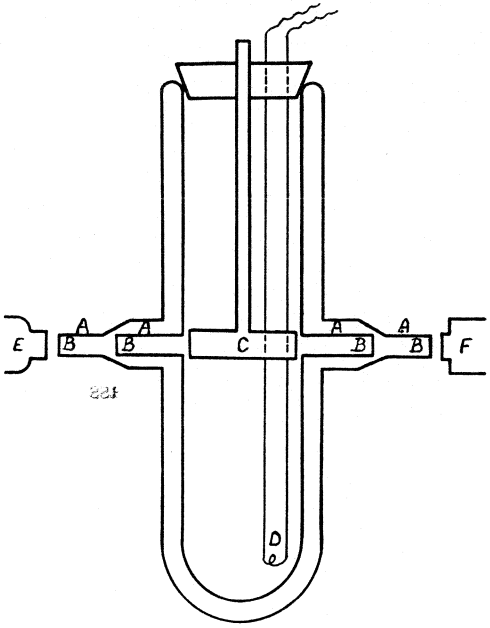


Fig. 1.

In the following a short résumé is given of the more essential points in the preparation and purification of the compounds and solvents used.

Purification of Solvents

Propane.—Gaseous propane from a commercial cylinder was passed successively through spiral wash bottles containing 15% fuming sulfuric acid, concentrated sulfuric acid, saturated permanganate solution containing 10% sodium carbonate, dilute potassium hydroxide solution, and a drying tower filled with sticks of solid potassium hydroxide. It was condensed by solid carbon dioxide.

Pentane.—Shell Pentane Solvent was shaken with saturated potassium permanganate solution containing 10% sodium carbonate until it no longer reduced the permanganate solution. It was then successively washed with water, dilute sulfuric acid and concentrated sulfuric acid. To remove aromatic hydrocarbons the pentane was shaken for four hours with one-fourth its volume of 15% fuming sulfuric acid. After this it was successively washed with concentrated sulfuric acid, dilute sulfuric acid, 10% sodium carbonate solution and finally with distilled water. The pentane was dried over calcium chloride and distilled over sodium. The material all boiled under 34°. It was tested spectrographically for transparency and if any bands persisted the fuming sulfuric acid treatment was repeated. The original material was of such purity that purification was readily obtained. The solvent used was transparent to 2250 Å., which was the limit of the complete apparatus when empty.

Preparation and Purification of Compounds

Benzene.—Eastman thiophene-free benzene was dried over sodium and distilled through a five-foot column. The boiling point was 80.4°.

$\Delta^{1,3}$-Cyclohexadiene.—This was prepared by removing hydrogen bromide from 1,2-dibromocyclohexane with sodium ethylate according to Hoffmann and Damm.[6] The product was repeatedly distilled over sodium in a stream of carbon dioxide until the refractive index[7] was n_D^{20} 1.4740 ± 0.0002 and the boiling point was 80.25–80.75°.

Cyclohexene.—Eastman cyclohexene was repeatedly distilled over sodium through a silver spiral fractionating column until a constant absorption spectrum was obtained. The spectrum shows no structure.[8]

Dimethylbutadiene.—This compound was prepared from pinacol. The product was redistilled over sodium until its boiling point was 68.8–69.4°.

Benzaldehyde.—Commercial benzaldehyde was purified through the bisulfite derivative. The sample taken boiled at 66° (10 mm.).

Phenylacetaldehyde.—Phenylacetaldehyde diethyl acetal was prepared and hydrolyzed to phenylacetaldehyde after the method of Woods and Comley.[9] The aldehyde boiled at 195–198° at atmospheric pressure. The semicarbazone melted at 152° and the oxime at 93–95°. The aldehyde was purified through the bisulfite derivative from which it was regenerated by steam distillation from a solution made slightly alkaline with sodium carbonate.

Hydrocinnamic Aldehyde.—Eastman hydrocinnamic aldehyde was purified through the bisulfite derivative. The sample taken boiled at 106–108° (10 mm.).

Chlorobenzene.—C. P. chlorobenzene was redistilled until its boiling point was 132°.

Benzyl Chloride.—Eastman benzyl chloride was redistilled several times. The fraction boiling at 176–179° was filtered through activated charcoal, dried over calcium chloride and distilled again. The sample taken boiled at 178–178.5°.

β-Phenylethyl Chloride, γ-Phenylpropyl Chloride, δ-Phenylbutyl Chloride and ω-Phenylheptyl Chloride.—The preparation of these compounds has been described by Conant and Kirner.[10] The samples were generously loaned by Professor J. B. Conant.

Results and Discussion

It seemed desirable to investigate the relation between the width of absorption bands and molecular structure using the simplest and most similar representatives of the aromatic and aliphatic series. As such, benzene, cyclohexadiene, cyclohexene and dimethylbutadiene were chosen. At room temperature benzene possesses fairly sharp bands while cyclohexadiene has only one wide band according to the work of Stark,[11] which we were able to confirm. The other two compounds show only a gradually increasing absorption toward the short wave lengths. Figure 2 presents microphotometer records[12] of the spectra of the first two compounds at

[6] Hoffmann and Damm, *Mitt. schles. Kohlenforschungsinst. Kaiser-Wilhelm-Ges.*, **2**, 97–146 (1927); *Chem. Abstracts*, **22**, 1249 (1928).

[7] Hoffmann and Damm[6] reported n_D^{20} 1.4755 and Willstätter, *Ber.*, **45**, 1464 (1912), reported n_D^{20} 1.47439.

[8] Stark and Lipp, *Z. physik. Chem.*, **86**, 43 (1913).

[9] Woods and Comley, *J. Soc. Chem. Ind.*, **42**, 429T (1923).

[10] Conant and Kirner, THIS JOURNAL, **46**, 241 (1924).

[11] Stark and Levy, *Jahr. Radioakt. Electronik.*, **10**, 179 (1913).

[12] We take this opportunity to thank Professor Plaskett of the Harvard Observatory for permission to use the Moll microphotometer belonging to the Observatory.

liquid nitrogen temperature. Cyclohexene and dimethylbutadiene are not shown as no significant changes have been obtained on cooling. The reproduction brings out clearly the sharpness of the benzene bands[13] and also the resolution of the cyclohexadiene absorption into three bands. The half width of the bands in the two spectra is, however, strikingly different, being *ca.* 130 cm.$^{-1}$ for benzene and about 700 cm.$^{-1}$ for the other compound. This difference seems to be quite general and the literature presents no evidence, which we could locate, of bands observed with aliphatic compounds in solution which even approach the narrowness of benzene bands. The acetaldehyde absorption spectrum, which is resolved into

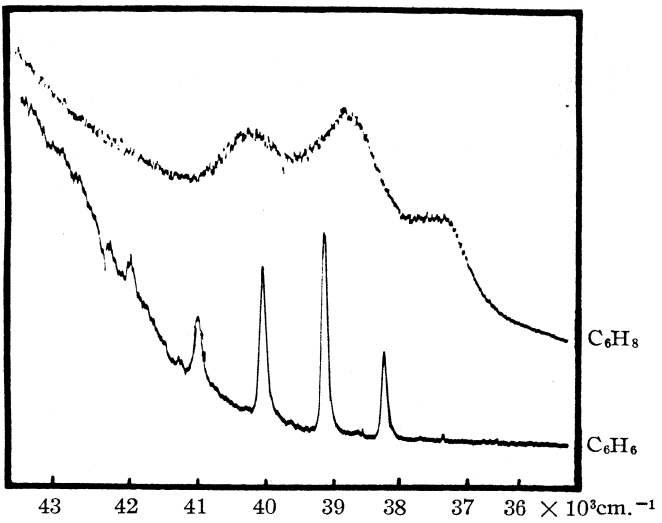


Fig. 2.

seven component bands at liquid air temperature (see Fig. 3, A) has half-widths of about 400 cm.$^{-1}$. About the same half-width persists in the spectra of the carbonyl group attached to the benzene ring (Fig. 3), while the latter retains the narrow bands practically unchanged in their width in all derivatives which we investigated. Various publications dealing with the spectra of aromatic compounds at room temperature indicate that this behavior is typical of other derivatives of benzene and other aromatic carbon rings, showing that a significant difference exists between their spectra and those of aliphatic compounds. This difference, however, is not the absence of bands, as assumed by Hartley, but their different half-width.

At 80°K. the rotational energy of molecules is so small that on this

[13] Fainter but similarly narrow bands located between the strong ones have been observed visually on our other photographs of the benzene spectrum (see also Kronenberger[3]).

account alone vibrational bands should all appear at least as sharp as those of benzene, particularly so long as only compounds of approximately the same molecular weight are compared. The unequal width observed is due therefore to other causes. One of these, probably the most important, is that many aliphatic compounds have in the vapor phase only continuous or diffuse spectra owing to photochemical dissociation and predissociation. These spectra, of course, cannot show structure in solution no matter how low the temperature. It is somewhat doubtful, though, whether this explanation suffices for those cases, like cyclohexadiene or the carbonyl group, where vibrational structure is obtained in the liquid state and where at least the long wave length part of the gaseous spectrum is discrete.[14]

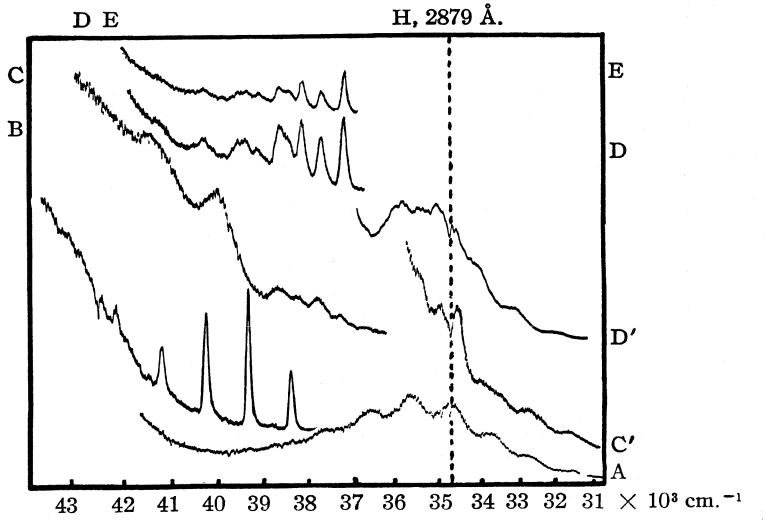


Fig. 3.

It seems more probable that in solution the fields of the surrounding molecules cause considerable broadening of the absorption bands by disturbing the electronic levels. The work of Kronenberger[3] also points to this. He found by direct comparison that the bands of benzene in solution are more diffuse than those of benzene crystals. In the latter case, owing to the regular spacing of the molecules, the broadening should be reduced to a minimum. The present work shows that the disturbing influence of the solvent is much greater with aliphatic compounds whether they be small atomic groups or even rings with double bonds. Thus the electronic states in aromatic rings appear to be exceptionally stable against external influences. Perhaps this can be adduced in favor of the central bond theory for such molecules, since neither the ring structure, nor the

[14] V. Henri, "Structure des Molecules," Paris, 1925.

conjugated double bond, both being present in cyclohexadiene, show this phenomenon. At any rate the present experiments indicate that the sharpness of absorption bands in solution can be utilized as a supplementary method in investigating the structure of large molecules and thus completely confirm the conclusions reached in a recent communication by Conant and Kamerling.[15]

Although the problem of mutual influence of spectra by two groups in a molecule has already received considerable attention, some new evidence on the subject seemed to be desirable and with this purpose in view a series of aryl aromatic aldehydes has been chosen together with some aryl aromatic monochlorides. The choice was guided by the consideration that the carbonyl group and the benzene ring both have well-defined and not overlapping absorption spectra in an easily accessible spectral region.

The spectra obtained at low temperatures, although considerably sharper and showing more fine structure than those reported previously from the work at room temperature, proved to be insufficiently resolved for an attempt at vibrational analysis. Accordingly in Table I are reported only the wave numbers of the observed bands, while Fig. 3 brings out the salient points and shows the microphotometer records of the spectra of acetaldehyde (A), benzene (B), phenylacetaldehyde (C) and (C′), hydrocinnamic aldehyde (D) and (D′), and phenylheptyl chloride (E). Turning first to the absorption of the benzene ring it will be seen that the substitution of a carbonyl group produces profound changes in the vibra-

TABLE I

WAVE NUMBERS OF OBSERVED BANDS

Bands, cm.$^{-1}$	Half width cm.$^{-1}$	Bands, cm.$^{-1}$	Half width, cm.$^{-1}$	Bands, cm.$^{-1}$	Half width, cm.$^{-1}$
Phenylacetaldehyde		Hydrocinnamic aldehyde		Phenylbutyl chloride*	
30490	500	32010	400	36660	
31630	540	33150	330	37110	
32770	580	34160	340	37360	
33800		35150		37880	
34590		35970		38290	
35000		37260	150	38570	
35190		37720	130	38760	
35460	200	38150	150	39220	
36750	140	38340	100	39430	
37340	110	38620	130	39670	
37750	210	39060	150	39780	
38290	130	30370	130	39980	
38690		30490	150	40140	
39870		40290		40340	
41430		41240		41190	

[15] Conant and Kamerling, THIS JOURNAL, **53**, 3522 (1931).

TABLE I (*Concluded*)

Bands, cm.$^{-1}$	Half width cm.$^{-1}$
Benzene	
37790	120
38410	120
39270	140
40200	140
41200	120
42160	110
42410	110
Cyclohexadiene	
37310	620
38910	780
40210	730
Benzaldehyde	
26940	
27560	170**
28270	220**
29020	150**
29440	270**
30550	490*
31660	460**
32820	470**
34510	200
34950	150
35290	150
35640	150
36620	100
38340	
39700	
41000	
Acetaldehyde	
30500	
31510	400
32780	
33800	410
34780	510
35710	480
36600	500
37290	350

Bands, cm.$^{-1}$	Half width cm.$^{-1}$
Propionaldehyde	
30490	370
32070	360
33210	350
34250	360
35160	410
36190	370
37270	340
38380	320
Chlorobenzene	
36870	
37410	
37850	
38310	
38810	
39260	
39830	
40290	
40870	
41930	
Phenylethyl chloride*	
37410	
37880	
38310	
38630	
38870	
39050	
39280	
39510	
39740	
40420	
40770	
41000	
41310	
42460	

Bands, cm.$^{-1}$	Half width cm.$^{-1}$
Benzyl chloride*	
34630	
34870	
36890	
37400	
37610	
37790	
38310	
38570	
39280	
39430	
39830	
Phenylpropyl chloride*	
36940	
37400	
37880	
38300	
38570	
38780	
39030	
39200	
39460	
39730	
39980	
40180	
40440	
41240	
Phenylheptyl chloride	
37190	110
37710	150
38120	140
38310	120
38600	130
39050	100
39320	130
39480	100
40230	340
41250	400 (?)

Bands for compounds marked with (*) are computed from comparator measurements and in the case of benzaldehyde half-widths are estimated by comparison with bands of known half-width on other plates; benzaldehyde bands marked (**) are from a microphotometer record of this section of the benzaldehyde spectrum. Heptyl aldehyde shows within the limits of experimental error the same absorption spectrum as propionaldehyde. The benzaldehyde band marked (*), judging from the microphotometer record, is comprised of two bands with half-width about 200 cm.$^{-1}$.

tional structure, as should have been expected from the altered symmetry conditions alone. Further changes are produced by interposing one and two —CH_2— groups between the carbonyl group and the ring, but at this stage the spectrum has reached its final form, as can be noticed by comparison with phenylheptyl chloride, both being identical in so far as the positions of the bands are concerned.

Similar conclusions are reached with respect to the absorption of the carbonyl group. Considerable alterations in the band positions occur until two CH_2 groups have been introduced between the aldehyde group and the benzene ring (A, C′, D′ in Fig. 3), or—in case of aliphatic aldehydes—until the carbon chain is two atoms long. With longer chains the carbonyl absorption spectrum remains practically unchanged. Thus the bands belonging to hydrocinnamic, propionic and heptyl aldehydes have identical positions within the experimental errors of their determination, but with benzaldehyde the carbonyl spectrum is shifted to the visible somewhat and the bands are narrower.

Purvis[16] pointed out some time ago that the mutual influence of the groups on their respective spectra decreases as their spacing in the molecule increases. The present work confirms this conclusion and gives it a more precise illustration in the case of the aromatic aldehydes, which show that a very short interposed carbon chain suffices to make the vibrations and the electronic levels of the two groups quite independent of each other. Attention may be called to the fact that this distance of two —CH_2— groups nearly coincides with the distance at which two such groups as carbonyl and halogens cease to affect appreciably their respective chemical properties in the straight chain compounds. The frequencies of the Raman lines attributed to vibration of certain atomic linkages also cease to be appreciably influenced by the size of the remainder of the molecule when the attached carbon chain is longer than two or three atoms.

In conclusion we wish to express our appreciation for the useful suggestions of Professor J. B. Conant, which have added greatly to the success of this work. We are much indebted to the Cyrus M. Walker Fund of the American Academy of Arts and Sciences for a grant which enabled us to purchase a spectrograph used throughout this work.

Summary

1. An apparatus is described for studying the ultraviolet absorption spectra in solution at low temperatures.

2. It is shown that aromatic rings are characterized by narrow absorption bands in solution at low temperatures, while the spectra of aliphatic groups remain diffuse.

[16] Purvis, *J. Chem. Soc.*, **99**, 2318 (1911); **127**, 9 (1925). This phenomenon was also noticed by Baly and Collie, *ibid.*, **87**, 1332 (1905).

3. The mutual influence of the spectra of two such groups as the carbonyl and benzene rings extends through carbon chains not more than two atoms long. At greater distances in the molecule the spectra become entirely independent of each other.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID. IV. THE PERCHLORATO-CHLOROPLATINATE METHOD FOR THE DETERMINATION OF POTASSIUM IN THE PRESENCE OF SODIUM

BY G. FREDERICK SMITH AND A. C. SHEAD[1]

RECEIVED OCTOBER 22, 1931 PUBLISHED MAY 7, 1932

Introduction

The separation and determination of potassium in the presence of sodium and lithium are most commonly carried out following the semi-extraction process of Fresenius.[2] Chloroplatinic acid is used to convert the aqueous solution of the mixed chlorides to the corresponding chloroplatinates, followed by the extraction of sodium and lithium chloroplatinates with ethyl alcohol to produce 80–85% of the latter. Many advantages result from the use of lithium chloroplatinate in place of chloroplatinic acid in the separation of potassium from sodium by the Fresenius process as shown by the present authors.[3] Very distinct improvements in the perchlorate method in the separation of potassium from sodium have been developed as a result of previously published research from this Laboratory[4] which seem to justify claims of superiority for the perchloric acid method over the chloroplatinate separation. In addition the use of perchloric acid facilitates the separation of sodium from lithium.[5]

The present paper demonstrates the advantage resulting from the simultaneous application of both perchloric and chloroplatinic acids to the separation and determination of potassium in the presence of sodium. Four distinct advantages result from this method of attack. Only enough chloroplatinic acid is employed to convert the potassium present to potas-

[1] Holder of "The J. T. Baker Chemical Company Fellowship in Analytical Chemistry" for the year 1930–1931. Submitted in partial fulfilment of the requirements for the Ph.D. degree in the Graduate School of the University of Illinois by the junior author.

[2] Fresenius, *Z. anal. Chem.*, **15**, 224 (1876); **16**, 63 (1877); **21**, 234 (1882).

[3] Smith and Shead, THIS JOURNAL, **53**, 947 (1931).

[4] Smith, *ibid.*, **45**, 2073 (1923); **47**, 762 (1925). Smith and Ross, *ibid.*, **47**, 774 (1925); **47**, 1020 (1925).

[5] Willard and Smith, *ibid.*, **44**, 2816 (1922).

sium chloroplatinate. Following the Fresenius process the sodium must be converted to sodium chloroplatinate to take advantage of its solubility in alcohol. Since the ratio of chloroplatinic acid to sodium chloride, $H_2PtCl_6 \cdot 6H_2O/2NaCl$, is approximately 4.8, the saving in platinum is apparent. A second improvement is that the process is completely a precipitation process and not, as with the Fresenius scheme, a semi-extraction method. Occlusion of sodium salts by the precipitated potassium chloroplatinate is therefore minimized. A third improvement results from the weighing of a mixture of potassium and sodium perchlorates in place of the corresponding chlorides. Lastly, as already shown,[2] the precipitated potassium chloroplatinate is stable after drying at 300–350°. Any error resulting from the occlusion of solvent by the potassium chloroplatinate is thus eliminated and the time required for its drying greatly reduced.

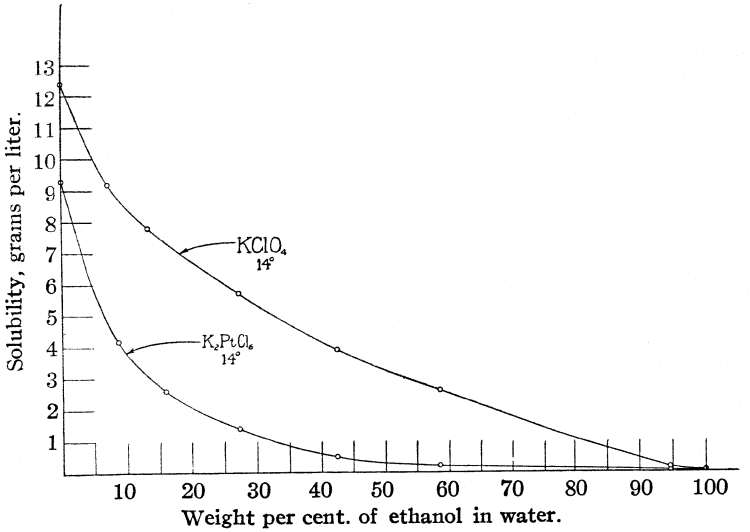


Fig. 1.—The solubility of K_2PtCl_6 and $KClO_4$ in alcohol–water solutions.

The Method

The process in brief is as follows.

The mixture of potassium and sodium chlorides obtained following the application of the J. Lawrence Smith method for decomposing an insoluble silicate (or a mixture of potassium and sodium nitrates) is converted to perchlorates by evaporation to dryness in a platinum dish or crucible with an excess of 70–72% perchloric acid. A 30-cc. Pyrex beaker may be used for the evaporation. The mixed perchlorates of potassium and sodium are dissolved by heating with a few cubic centimeters of water and again evaporated to dryness and heated for fifteen to thirty minutes at 350°, cooled and weighed. Anhydrous sodium perchlorate is faintly hygroscopic and the container plus the sample should be weighed covered.

The mixture of potassium and sodium perchlorates is dissolved in hot water (5 cc.

is sufficient for all ordinary samples) and 5 cc. of 95% or stronger ethanol is added and the solution warmed to just below the boiling point. Small portions of a 10% solution of chloroplatinic acid dissolved in ethanol are added until potassium chloroplatinate begins to precipitate. After digesting for a minute at just below the boiling point, the slow addition of precipitant is continued until all the potassium present is precipitated and the supernatant liquid is colored slightly yellow. Enough ethanol is added to make an 80–85% concentration of alcohol (not less than 30 cc. of alcohol in case 5 cc. of water was used) and the solution is digested for five minutes on an electric hot-plate with stirring at just below the boiling temperature. The precipitate and solution are cooled to room temperature, filtered, washed with 85% or stronger alcohol and the filtrate set aside for recovery of the slight excess of platinum used or for the direct determination of sodium. The filtering crucible and precipitate are dried for five minutes at 100–130° to remove the alcohol and finally for fifteen minutes at 300–350°, cooled and weighed. The potassium chloride originally present is calculated using the theoretical factor $2KCl/K_2PtCl_6 = 0.3067$.

Solubilities Involved in the Perchlorato-Chloroplatinate Process.— Five cubic centimeters of water at 25° dissolves more than 10 g. of sodium perchlorate. The addition of alcohol in equal proportion does not greatly diminish this solubility. Lithium perchlorate is less soluble in water (2.98 g. in 5 cc.) but is much more soluble in ethyl alcohol than is sodium perchlorate. The comparative solubilities of potassium perchlorate and potassium chloroplatinate in various strengths of aqueous ethanol are given in Table I taken from the data of M. Pierrot.[6]

TABLE I

THE COMPARISON IN SOLUBILITY OF POTASSIUM PERCHLORATE AND POTASSIUM CHLOROPLATINATE IN VARIOUS CONCENTRATIONS OF AQUEOUS ETHANOL AT 14°

Material	Concentration of ethanol, % by weight of alcohol									
	0.0	7.1	8.7	13.2	15.9	27.3	42.4	58.5	94.7	100
	Solubility g./1000 cc.									
$KClO_4$	12.4	9.2		7.8		5.7	3.9	2.6	0.15	0.071[a]
K_2PtCl_6	9.3		4.2		2.6	1.4	0.5	0.2	0.02	0.018[a]

[a] Solubility determinations in absolute alcohol: $KClO_4$ by Willard and Smith, THIS JOURNAL, **45**, 286 (1923). Solubility of K_2PtCl_6 calculated from accepted solubility data, 1 part of K_2PtCl_6 to 42,600 parts of ethanol.

From an examination of Table I it will be observed that the solubility of potassium chloroplatinate in water is very highly suppressed with increasing addition of ethyl alcohol as compared to the diminution in the solubility of potassium perchlorate under the same conditions. For solutions of equal parts of ethyl alcohol and water, 32.5 mg. of potassium perchlorate dissolves in 10 cc. This amount is increased approximately ten-fold at the boiling point of such solutions.

Potassium chloroplatinate is so slightly soluble in a 50% solution of ethyl alcohol in water (4 mg. in 10 cc.) that this concentration was chosen for the first addition of chloroplatinic acid. It was found that the temperature coefficient of increase in solubility of potassium chloroplatinate

[6] Pierrot, *Compt. rend.*, **172**, 1041 (1921).

with increase in temperature is very slight. No need for excess of chloroplatinic acid for its common ion effect in reducing the solubility of potassium chloroplatinate is shown by the data. The addition of alcohol serves as an effective substitute when above 80%.

Preparation of Materials for Use in Testing the Accuracy of the Perchlorato–Chloroplatinate Process

Perchloric Acid.—Chemically pure 70–72% material distilled *in vacuo* and supplied by the G. Frederick Smith Chemical Company of Columbus, Ohio.

Potassium Chloride.—A portion of the same stock previously described[2] and demonstrated to be 100% pure. The fused product only was employed to eliminate the possibility of occluded moisture.

Sodium Chloride.—Samples were taken from a stock used in previous investigations published from this Laboratory. It had been repeatedly crystallized from water solution by the addition of gaseous hydrochloric acid with intermediate filtrations using centrifugal drainage. This preparation had been carried out by Dr. T. R. Ball, at present at Washington University, St. Louis, and was fused before weighings to eliminate the possibility of occluded moisture.

Chloroplatinic Acid.—Purchased from two different laboratory chemical supply houses and used as received.

Ethyl Alcohol.—Anhydrous alcohol as purchased in the market.

The Stability of Chloroplatinic Acid in Hot Alcoholic Solution.—The platinum in a hot alcoholic solution of chloroplatinic acid might be reduced to a lower stage of valence or to metallic platinum especially in the presence of reducing agents such as traces of aldehydes commonly present in alcohol. This possibility in the present method is practically eliminated for two reasons: first, the negligible increase in solubility of potassium chloroplatinate in hot as compared to cold alcohol solutions and second, the use of such a slight excess of chloroplatinic acid the latter being unnecessary either to convert sodium perchlorate to sodium chloroplatinate or for the common ion effect of excess precipitant. Samples of commercial anhydrous ethyl alcohol or the more common 95% alcohol either untreated or dried with lime followed by metallic calcium serve equally as well for this method. No determinations were lost because of the reduction of the chloroplatinic acid. Qualitative tests in all these types of alcohol showed traces of aldehyde or similar reducing agents.

Filtrates from the precipitation of potassium chloroplatinate containing sodium perchlorate, a slight excess of chloroplatinic acid and perchloric acid, when diluted further with water and allowed to digest for periods of thirty to sixty minutes at steam-bath temperature, precipitate their platinum completely as platinum black, a reduction conveniently employed in the direct determination of sodium. The filtrate from the potassium separation is so treated, the platinum filtered and washed and the sodium perchlorate determined by conversion to sulfate or by precipitation as sodium chloride following the method of Willard and Smith,[5]

Smith and Ross[4] or by direct weight as sodium perchlorate as described in the next section.

The Conversion and Determination of Sodium Chloride as Sodium Perchlorate and its Stability at 350°.—By comparison of the two conversion factors, $Na_2O/2NaCl$ (0.5303) and $Na_2O/2NaClO_4$ (0.2531), weighing sodium as perchlorate instead of chloride is seen to carry a distinct advantage. Conditions for the correct determination of potassium as perchlorate have been clearly demonstrated by Smith and Ross.[4] To avoid a contamination of potassium perchlorate by either occluded perchloric acid or moisture it must be dried at 350°. If sodium perchlorate can be shown to be stable at 350°, and suitable for weighing in this form, the mixture of sodium and potassium chlorides, frequently weighed after drying at 500°, can be weighed more satisfactorily in the form of perchlorate. This becomes more important since it is recognized that weighing mixtures of sodium and potassium chlorides following drying below their fusion temperature does not eliminate moisture. At the melting point these chlorides are too volatile to permit this treatment without prohibitive loss in weight. It is obvious that an indirect determination of sodium by difference is unsatisfactory for precise work. This practice is, however, commonly applied since the potassium determination is more important than that of sodium. The following experiments in the conversion of sodium chloride to perchlorate for final weighing are, therefore, described.

Weighed samples of pure sodium chloride were placed in a 30-cc. Pyrex beaker, dissolved in water and a small excess of pure 70–72% perchloric acid added. The samples were evaporated dry and the excess perchloric acid expelled. After heating during two and one-half hours in an electric muffle at 350°, the samples were cooled in a desiccator and weighed. In the latter operation a small watch-glass was used as a beaker cover. The results are shown in Table II. Sodium perchlorate crystallized from solution above 30° in the form of the anhydrous salt. A monohydrate is obtained by crystallizing from solution below 25°. The transition point

TABLE II

THE CONVERSION OF SODIUM CHLORIDE TO PERCHLORATE WITH DRYING AT 350°

NaCl taken, g.	$NaClO_4$ found, g.	$NaClO_4$ calcd., g.	Error in $NaClO_4$, g.	NaCl taken, g.	$NaClO_4$ found, g.	$NaClO_4$ calcd., g.	Error in $NaClO_4$, g.
0.2013	0.4217	0.4217	0.0000	0.2496	0.5234	0.5228	+0.0006
.3098	.6493	.6490	+ .0003	.3993	.8375	.8365	+ .0010
.3371	.7069	.7062	+ .0007	.0804	.1688	.1684	+ .0004
.3376	.7074	.7072	+ .0002	.0428	.0899	.0898	+ .0001
.1985	.4160	.4158	+ .0002	.0979	.2045	.2051	− .0006
.3941	.8285	.8286	+ .0002	.1367	.2863	.2864	− .0001
.3460	.7258	.7248	+ .0010	.2293	.4805	.4804	+ .0001
						Av.	+ .0002

lies between these limits. It is easy, therefore, to favor the formation of the anhydrous salt and thus avoid its subsequent dehydration. The time of drying at 350° was purposely and unnecessarily extended to completely test the stability of sodium perchlorate. The melting point of sodium perchlorate is 482°.

The Determination of Potassium Chloride Using the Perchlorato-Chloroplatinate Process.—Samples of fused C. P. potassium chloride were weighed and dissolved in a few cc. of hot water in a 150-cc. beaker and converted to perchlorates by evaporation to dryness following the addition of 2 cc. of 70% perchloric acid. The samples were again dissolved by the addition of a few cc. of hot water and a second time evaporated dry and heated finally over a wire gauze to remove the last trace of occluded perchloric acid. The potassium perchlorate was then dissolved in a known volume of 50% ethyl alcohol, warming on the hot-plate nearly to the boiling point to limit the volume of solvent required. The samples were then precipitated as potassium chloroplatinate by the addition of reagent in several portions, with intermediate digestion for a minute on the hot-plate at just below the boiling point. The alcohol used to dissolve the chloroplatinic acid was sufficient to make a final alcohol concentration greater than 80%. Excess of precipitant is easily recognized by the appearance of a yellow color in the solution being precipitated. After five minutes' digestion during precipitation, the solutions and precipitates are cooled to room temperature and filtered using a platinum Monroe filtering crucible or a sintered quartz or glass filtering medium. The precipitates were washed with absolute alcohol and dried for twelve hours at 135° and finally for fifteen minutes at 350°, cooled, dried and weighed after each treatment. The chloroplatinic acid was added in weighed amount calculated to give a 10% excess and the excess platinum finally determined in the filtrates from the potassium separation as previously described. The results of these analyses in the absence of sodium are given in Table III.

TABLE III

THE PRECIPITATION OF POTASSIUM CHLOROPLATINATE FROM PERCHLORATE SOLUTION USING CHLOROPLATINIC ACID AND ETHYL ALCOHOL

KCl taken, g.	$KClO_4$ soln. in 50% alcohol, cc.	H_2PtCl_6 $6H_2O$ used, g.	Pt in filtrate Metal, g.	Pt in filtrate Acid calcd., g.	Potassium chloroplatinate 135°, g.	Potassium chloroplatinate 350°, g.	Filtrate and washings, cc.	Loss in wt. of K_2PtCl_6, 135° → 350° mg.	Loss in wt. of K_2PtCl_6, 135° → 350° %	KCl found, g.	Error, mg.
0.07775	8	0.35	0.0315	0.0836	0.25075	0.2504	42.5	0.35	0.14	0.07685	−0.8
.1347	8	.55	.0254	.0674	.43965	.43895	43.6	0.65	.15	.1347	.0
.30455	16	1.2	.0495	.1311	.99195	.99175	66.2	1.20	.12	.30435	− .2
.1216	8	0.5	.0143	.0379	.39775	.3971	48.8	0.75	.19	.1219	+ .3
.1887	14	.85	.0741	.1963	.6155	.6151	54.1	.60	.10	.1888	+ .1
Mean solubility of K_2PtCl_6, 0.84 mg./100 cc.						Av.	51 cc.		0.14%		−0.12

It will be seen from the results of Table III that using a perchlorate solution, chloroplatinic acid precipitates potassium chloroplatinate equal in purity to that produced by lithium chloroplatinate in chloride solutions of potassium.[3] The precipitated potassium chloroplatinate in the former case differs from the latter only in the formation of free perchloric acid in place of hydrochloric acid. The presence of hydrochloric acid is also thus proved to cause impure precipitates of potassium chloroplatinate by the original Fresenius method. Potassium chloroplatinate is not free from moisture after drying at 135° for twelve hours. Results obtained by dry-

ing for fifteen minutes at 350°, or to constant weight, show that precipitates dried at the lower temperature contain an average of 0.12% occluded solvent. Using chloroplatinic acid as above described, determinations of potassium, sodium and lithium from the same sample can be obtained, which is not true using lithium chloroplatinate. A distinctive feature incorporated in the present method lies in the fact that absolute alcohol can be employed to transfer and wash precipitates of potassium chloroplatinate. This is not possible by the Fresenius method because of the formation of sodium chloride from sodium chloroplatinate. Assuming an average case with 50 cc. of filtrate and washings, only 0.14 mg. of potassium chloride remains unprecipitated, corresponding to 0.08 mg. of potassium oxide. Drying precipitates of K_2PtCl_6 obtained by this method at 135° instead of 350° gives high results almost exactly compensating for the loss of potassium due to solubility.

The Separation of Potassium in Presence of Sodium from Solutions of their Perchlorates Using Chloroplatinic Acid.—Samples of mixtures of weighed portions of potassium and sodium chlorides were converted to perchlorates and prepared for the determination of potassium in exactly the same manner as described in connection with Table III. Potassium chloroplatinate was precipitated in the same manner using a 10% excess of chloroplatinic acid and the precipitates filtered and washed with absolute alcohol and dried for five minutes at 135° and for fifteen minutes at 350°. Results are given in Table IV, calculated from the weight of K_2PtCl_6 using the factor 0.3067 (theoretical).

TABLE IV

THE SEPARATION OF POTASSIUM FROM SODIUM IN ALCOHOLIC PERCHLORATE SOLUTION USING CHLOROPLATINIC ACID

KCl taken, g.	NaCl taken, g.	K_2PtCl_6, g.	KCl found, g.	Filtrate and washings, g.	Error, KCl, mg.
0.13475	0.2018	0.43725	0.1342	38	−0.55
.1095	.1086	.3572	.1096	42	+ .1
.0633	.3846	.2065	.0634	64	− .1
.0522	.2238	.1635	.0502	44	− .2
.02850	.1495	.0936	.0287	43	+ .2
.0037	.0083	.0113	.0035	..	− .2
.01625	.0174	.05215	.0160	..	− .25
.0279	.0228	.08965	.0275	..	− .4
.0609	.0333	.1954	.0599	..	−1.0
.08635	.1342	.2799	.0858	..	−0.55
.05085	.2293	.1643	.0504	..	− .45
.0333	.0979	.1109	.0340	..	+ .7
.0089	.0429	.0289	.0089	..	.0
.0170	.0045	.0558	.0171	..	+ .1
.02135	.1985	.07045	.0216	..	+ .25
				Av.	− .14

It is seen from the results of Table IV that the separation of potassium chloroplatinate in the presence of sodium gives as accurate a potassium determination as obtained in Table III in the absence of sodium. The method is accurate to an average of approximately 0.15% in both cases. It is interesting to note that for the combined determinations of Table IV, less than 3 g. of $H_2PtCl_6 \cdot 6H_2O$ was required, whereas, if the original Fresenius method had been used, approximately 12 g. would have been necessary. The method is very rapid as compared to the original Fresenius process both because of the method of precipitation and the short time (twenty minutes) required to dry the precipitated K_2PtCl_6. The precipitate is obtained as finely divided, light lemon-yellow colored crystals, which filter with ease and are very easily transferred from precipitating beaker to filtering crucible.

The Determination of Small Amounts of Potassium in Presence of Large Amounts of Sodium.—The present method requiring no conversion of sodium chloride to sodium chloroplatinate immediately suggests its application to the determination of small amounts of potassium in the presence of large amounts of sodium. This determination is generally possibly only in two operations. For example, the potassium present is concentrated by first precipitating as cobaltinitrite, $K_2NaCo(NO_2)_6$, followed by solution in hydrochloric acid and conversion to perchlorate.[7] The present method was therefore examined in the determination of less than 0.5% of potassium in sodium chloride. The results obtained indicated the need for further investigation of this subject for reasons indicated by the following equation

$$2KClO_4 + H_2PtCl_6 + x\ NaClO_4 \longleftrightarrow K_2PtCl_6 + 2H^+ + (x+2)\ ClO_4^- + x\ Na^+$$

As the amount of sodium perchlorate increases, the increase of perchlorate ions reaches sufficient magnitude to direct the reaction from right to left rather than the reverse and either the K_2PtCl_6 does not form at all or there is obtained a mixed precipitate of K_2PtCl_6 and $KClO_4$. Successful separations of 5 mg. of potassium chloride in the presence of 2000 mg. of sodium chloride were attempted. More data are being collected on this subject. No difficulty in applying the present method is encountered as long as the ratio of potassium chloride to sodium chloride is 1%, using a one-gram sample or less of the mixed chlorides. The attempt to follow out the present procedure (slightly modified in some instances) gave results shown in Table V.

Results given in Table V are seen to be satisfactory only in the case of the first two determinations. The adjustment of the present method to analyses in the range used in this table is now being investigated. No violent reactions were met with in the study of this method. Owing to the relatively high concentration of water present in all solutions of the per-

[7] Bennett, *Analyst*, **41**, 165 (1916).

TABLE V

THE DETERMINATION OF SMALL AMOUNTS OF POTASSIUM PRESENT WITH LARGE AMOUNTS OF SODIUM

5 cc. 70% $HClO_4$ used to convert chlorides to perchlorates. 0.12 g. of $H_2PtCl_6 \cdot 6H_2O$ used for each precipitation.

KCl taken, g.	NaCl taken, g.	Hot solvent used to dissolve mixed perchlorates H_2O + C_2H_5OH (Anhyd.), cc.	cc.	K_2PtCl_6, g.	KCl calcd., g.	Error, KCl, mg.
0.00935	1.2819	3	45	0.02965	0.0091	−0.25
.0053	1.4592	2	35	.01685	.0052	−0.1
.0158	1.4611	.	60	.00975	.00605	−3.0
.0189	1.9165	7	42	.04675	.0144	−4.5
.00545	1.9038	5	55	.01235	.0038	−1.7
.0044	2.1821	2	35	.00735	.0023	−2.1
.00465	2.0017	2	35	.01395	.0043	−0.35
.00125	1.2832	2	35	.00305	.0095	−0.3

chlorates in alcohol, no explosion is possible. Converting mixtures of sodium and potassium chlorides or nitrates to perchlorates by evaporation with perchloric acid to dryness is perfectly safe. This method should, therefore, not fail of application because of prejudice from this source.

Summary

1. Potassium and sodium in the form of their perchlorate solution in 50% ethyl alcohol and water mixture may be precipitated by the addition of an alcoholic solution of chloroplatinic acid and the potassium quantitatively separated in the form of potassium chloroplatinate.

2. Since sodium perchlorate is soluble in alcohol, only enough chloroplatinic acid is required to react with the potassium, thus effecting a saving in cost.

3. The method gives precipitates of theoretical composition stable upon drying at 350°.

4. Stronger alcoholic solutions may be used by this method than are possible starting with the mixed alkali chlorides. Anhydrous alcohol can be used to wash the precipitate.

5. Sodium and potassium can be weighed with advantage as mixed perchlorates after heating at 350°.

6. This is a precipitation process, not a semi-extraction method, and, therefore, more efficient.

7. Platinum is recovered from the filtrates by simply digesting for thirty to sixty minutes at 80–90°. The direct determination of sodium is thus facilitated.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HYDROGEN, CHLORINE, HYDROGEN CHLORIDE EQUILIBRIUM AT HIGH TEMPERATURES

BY W. F. GIAUQUE AND ROY OVERSTREET

RECEIVED OCTOBER 28, 1931 PUBLISHED MAY 7, 1932

The experimental investigation of chemical equilibria presents many difficulties. For gaseous equilibria nearly all of these are avoided when spectroscopic data are available for such determinations. Since the energy levels of molecules are independent of temperature the troublesome matters of temperature control and accurate measurements are eliminated. Moreover, even the higher energy levels may be excited for observation under conditions where the gas remains at conservative temperatures. Questions as to whether equilibrium has been reached, or if reached been shifted by quenching, do not enter. The energy levels of gas molecules at moderate pressures are independent of equilibrium conditions and in fact are usually best investigated under conditions where the gases exist separately.

The necessary equations and an example of their application have been given previously.[1]

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2} R \ln M - \frac{5}{2} R \ln T + R \ln P - C - R \ln R - R \ln Q \qquad (1)$$

where $F^\circ = H^\circ - TS^\circ$ and the various symbols have their usual significance, the superscript referring to the standard state. E_0° is the energy of the molecules when all are in the lowest level ($T = 0°$K.). $Q = \Sigma\, p\, e^{-\epsilon/kT}$ the summation being taken over all energy levels that are occupied by appreciable numbers of molecules. p is the *a priori* probability of the level concerned. The values of all constants used are those given by the "International Critical Tables." $R = 1.9869$ calories per mole per degree. $C + R \ln R = -7.267$ calories per mole per degree.

The amount of calculation involved in the evaluation of Q by means of summing the individual Boltzmann terms is very considerable except for the lighter molecules and low temperatures. Thus one of the principal purposes of this paper is to discuss an approximation method by which Q may be evaluated without loss in accuracy.

The rotational levels of a diatomic molecule are usually represented with a high degree of accuracy by the expression

$$\epsilon_r = Bm^2 + Dm^4 + Fm^6 + \ldots \qquad (2)$$

where $m = j + {}^1/_2$ and j is the rotational quantum number. The terms Dm^4, Fm^6, etc., arise from the fact that molecules are not rigid. The effect of these terms becomes considerable at large values of m.

$$p = 2j + 1 = 2m$$

[1] (a) Giauque, THIS JOURNAL, **52**, 4808 (1930); (b) *ibid.*, **52**, 4816 (1930).

Then

$$Q = \Sigma 2me^{[-hc(Bm^2 + Dm^4 + Fm^6 + \ldots)]/kT}$$

$$= \Sigma 2me^{-Bhcm^2/kT} \cdot e^{-Dhcm^4/kT} \cdot e^{-Fhcm^6/kT} \ldots$$

$$= \Sigma 2me^{-Bhcm^2/kT}\left[1 - \frac{Dhcm^4}{kT} + {}^1/_2\left(\frac{Dhcm^4}{kT}\right)^2 \ldots\right]\left[1 - \frac{Fhcm^6}{kT} + {}^1/_2\left(\frac{Fhcm^6}{kT}\right)^2 \ldots\right]$$

$$= \Sigma 2me^{-Bhcm^2/kT}\left[1 - \frac{Dhcm^4}{kT} - \frac{Fhcm^6}{kT} + {}^1/_2\left(\frac{Dhcm^4}{kT}\right)^2 + \left(\frac{Dhcm^4}{kT}\right)\left(\frac{Fhcm^6}{kT}\right) + {}^1/_2\left(\frac{Fhcm^6}{kT}\right)^2 \ldots\right] \quad (3)$$

As a first approximation integration may be substituted for summation, thus

$$Qe^{-\epsilon_0 hc/kT} = \int_0^\infty 2me^{-Bhcm^2/kT}\,dm - \int_0^\infty \frac{2Dhc}{kT} m^5 e^{-Bhcm^2/kT}\,dm - \int_0^\infty \frac{2Fhc}{kT} m^7 e^{-Bhcm^2/kT}\,dm + \int_0^\infty \left(\frac{Dhc}{kT}\right)^2 m^9 e^{-Bhcm^2/kT}\,dm + \int_0^\infty 2DF\left(\frac{hc}{kT}\right)^2 m^{11} e^{-Bhcm^2/kT}\,dm \ldots. \quad (4)$$

The factor $e^{-\epsilon_0 hc/kT}$ which accompanies Q is due to the fact that the integrals assume zero m as the reference point of energy whereas the reference point which we are to use is one in which $m = {}^1/_2$. This is done since we believe it is preferable to confine our calculations to observable states.

Integrating

$$Qe^{-\epsilon_0 hc/kT} = \frac{kT}{Bhc}\left[1 - 2!\frac{D}{B^2}\left(\frac{kT}{hc}\right) - 3!\frac{F}{B^3}\left(\frac{kT}{hc}\right)^2 + \frac{4!}{2!}\frac{D^2}{B^4}\left(\frac{kT}{hc}\right)^2 + 5!\frac{DF}{B^5}\left(\frac{kT}{hc}\right)^3 \ldots.\right] \quad (5a)$$

However, as is well known, the substitution of an integral for the summation of discrete terms introduces a small error. A treatment of this problem for the case of rigid diatomic molecules has been given by Mulholland[2] and by Sutherland.[3]

They find

$$\Sigma 2me^{-Bhcm^2/kT} = \frac{kT}{Bhc}\left[1 + \frac{Bhc}{12kT} \ldots\right] \quad (6)$$

Investigation of the other integrals which are substituted for summations in Equation 4 shows that no appreciable error is introduced by this procedure. For example, it may be shown that

$$\Sigma 2m^5 e^{-Bhcm^2/kT} = \int_0^\infty 2m^5 e^{-Bhcm^2/kT}\,dm + \frac{31}{4032} + = \frac{2}{B^3}\left(\frac{kT}{hc}\right)^3 + \frac{31}{4032} + \quad (7)$$

in which the correction term may be shown to be negligible.

[2] Mulholland, *Proc. Camb. Philos. Soc.*, **24**, 280 (1928).

[3] Sutherland, *ibid.*, **26**, 402 (1930).

The effect of the correction $(B/12)\ (hc/kT)$ is small compared to the effect of molecular stretching. Applying the above correction to Equation 5a we obtain

$$Qe^{-\epsilon_0 hc/kT} = \frac{kT}{Bhc}\left[1 + \frac{B}{12}\left(\frac{hc}{kT}\right) - 2!\,\frac{D}{B^2}\left(\frac{kT}{hc}\right) - 3!\,\frac{F}{B^3}\left(\frac{kT}{hc}\right)^2 + \frac{4!}{2!}\,\frac{D^2}{B^4}\left(\frac{kT}{hc}\right)^2 + 5!\,\frac{DF}{B^5}\left(\frac{kT}{hc}\right)^3 \cdots\right] \quad (5b)$$

This equation leads to values of Q which are more accurate than our requirement of 0.001 calorie per degree per mole in F/T. Equation 5a may be used to obtain the first and second derivatives of Q which are required for the calculation of energy and entropy and for heat capacity, respectively.

Sutherland used Q and its derivative, from Equation 6, to compute the entropy of nitric oxide by a formula which will be mentioned later. His calculation, which was made only for the boiling point temperature where the assumption of rigidity is a fair approximation, gave a result different by 0.03 E. U. from that obtained by Johnston and Giauque,[4] who used the more accurate summation method. Since we could see no reason why Sutherland's method should not be accurate, a recalculation was made using his method and assumption and we find agreement with the value of Johnston and Giauque.

A comparison of the results of actual summations, which had previously been made, and values from the application of Equation 5a to hydrogen chloride is given in Table I, which also shows the relative importance of the corrections.

TABLE I

COMPARISON OF Q VALUES FOR HCl^{35} BY SUMMATION AND APPROXIMATION METHODS

T	$e^{\frac{hc\epsilon_{m=1/2}}{kT}}$	$\times \frac{kT}{Bhc} \times \left(1 + \frac{Bhc}{12\,kT} - \frac{D}{B^2}\frac{kT}{hc} - \text{etc.}\right)$	Q approx. $n = 1/2$	$Q\Sigma$ $n = 1/2$
1000	1.00374	$\times$ 66.825 $(1 + 0.00125 + 0.00684)$	= 67.618	67.618
2000	1.00187	$\times$ 133.651 $(1 + 0.00062 + 0.01386)$	= 135.84	135.85

Before proceeding to the calculation of the free energy it is necessary to consider the manner in which such calculations are affected by the existence of isotopic molecules. It has long been recognized that the thermodynamic consequences of isotopes affect the reactants and products concerned in a chemical reaction at or above ordinary temperature in such a way as virtually to cancel the free energy effect. Nevertheless, it has seemed worth while to present figures showing the actual magnitude of such effects. Usually, accurate band spectra data apply to the predominant isotopic molecule. However, this is sufficient since the corresponding levels for the others may be easily and accurately calculated from those of the predominant one. The method of making this calcula-

[4] Johnston and Giauque, THIS JOURNAL, 51, 3194 (1929).

tion has been carefully considered by Mulliken.[5] Since the law of force binding the molecule is independent of the particular isotope considered, it may be shown that the constant B in Equation 2 is inversely proportional to the reduced mass μ where $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$. D varies as μ^{-2} and F as μ^{-3}. In the case of vibrational levels where

$$\epsilon_v = (v + 1/2)\omega_e + (v + 1/2)^2 \chi_e\omega_e + (v + 1/2)^3 y_e\omega_e \qquad (8)$$

$\mu^{-1/2}$ occurs in each term to the same power as $(v + 1/2)$. Thus the first term varies as $\mu^{-1/2}$, the second as μ^{-1}, etc.

The Free Energy of Diatomic Chlorine.—For the Cl_2 molecule the calculation of the Q function was made for the Cl_2^{35-35} molecule and the values for the Q's of Cl_2^{35-37} and Cl_2^{37-37} were then obtained by the application of correction factors based on the above equations. We shall not give the details of the above calculation as it should not be necessary to duplicate it for other cases when the negligible extent to which isotopic differences affect the distribution of atoms is made apparent.

The molecular constants of the chlorine molecule are given in Table II. They were taken from the work of Elliott.[6]

B_v and D_v may be represented by the expressions

$$B_v = Be + \alpha(v + 1/2)$$
$$D_v = De + \beta(v + 1/2)$$

In computing the isotope effect α varies as $\mu^{-3/2}$ and β varies as $\mu^{-5/2}$.

TABLE II

CONSTANTS IN THE ENERGY EQUATION OF THE CHLORINE 35–35 MOLECULE IN CM.$^{-1}$

Normal State:

$$\epsilon_v = 564.9(v + 1/2) - 4.0(v + 1/2)^2$$
$$B_v = 0.2438 - 1.7 \times 10^{-3}(v + 1/2)$$
$$D_v = -1.815 \times 10^{-7} - 3.1 \times 10^{-9}(v + 1/2)$$
$$F_e = -9.4 \times 10^{-14}$$

First Electronic Level:

$$\epsilon_e = 17657.7$$
$$\epsilon_v = 261.1(v + 1/2) - 5.42(v + 1/2)^2$$

v	Bv	v	Bv	v	Bv
0	0.1625	5	0.1470	10	0.1297
1	.1594	6	**.1437**	11	**.1254**
2	.1563	7	**.1408**	12	**.1209**
3	.1532	8	**.1375**	13	**.1166**
4	.1501	9	.1341		

The values given in heavy type have been observed; the others were calculated.

The electronic level at 17657.7 cm.$^{-1}$ has been classified as a $^3\pi$ level by Mulliken.[7]

With λ type doubling there are six electronic series of rotation-vibration

[5] Mulliken, *Phys. Rev.*, **25**, 119 (1925).

[6] Elliott, *Proc. Roy. Soc.* (London), [A] **127**, 638 (1930).

[7] Mulliken, *Phys. Rev.*, **36**, 699, 1440 (1930); **37**, 1412 (1931).

levels. Some small doubt remains concerning the ${}^3\pi$ classification but the matter is of almost negligible importance in the present calculations since at 3000°K. the total contribution to $(F^\circ - E_0^\circ)/T$ is only 0.010 and is but 0.002 calorie per degree per mole at 2500°K. In considering the isotope effect we will make use of the reaction

$$Cl_2^{35-35} + Cl_2^{37-37} = 2Cl_2^{35-37}$$

From Equation 8 the zero point vibrational energy for each of the three molecules can be calculated. They were found to be 800.46, 778.56 and 789.60 cm.$^{-1}$, respectively. While the absolute accuracy of these values is not as great as the figures indicate, the relative accuracy is significant and thus the value of $\Delta E_0^\circ = 0.18$ cm.$^{-1}$ is reliable. Similarly, in obtaining the value of $(F^\circ - E_0^\circ)/T$ particular attention was paid to relative accuracy, thus giving a more reliable value of $\Delta(F^\circ - F_0^\circ)/T$ than can be obtained from our tables, to be given later.

The value of $\Delta(F^\circ - E_0^\circ)/T$ for 298.1°K. is -2.7549. Combining this with $\Delta E_0^\circ/T$ we find

$$K = \frac{[Cl_2^{35-37}]^2}{[Cl_2^{35-35}][Cl_2^{37-37}]}$$

from the equation $\Delta F^\circ/T = -R \ln K = -2.7549 + 0.0006$, $K_{298.1} = 3.9997$. If the isotopes of chlorine were without preference as to the type of diatomic molecule formed, the value of K would be exactly 4. It may be of interest to note that at the absolute zero all of the chlorine atoms would be combined into molecules of Cl_2^{35-35} and Cl_2^{37-37} type since $R \ln K = -\Delta E_0^\circ/O = -\infty$ for the above reaction. By the methods given above one could readily compute the manner in which the equilibrium would shift with decreasing temperature to approach this interesting condition. However, a knowledge of the nuclear spin of Cl^{37} would be necessary.

Since the calculated value of K agrees with 4 within the limits of accuracy of our tables it is evident that we need not consider the effect further.

In making the above calculation the effect of nuclear spin has been neglected since it has been proved by Gibson and Heitler[8] that cancellation of this effect occurs in such cases.

In preparing the tables to be given below we have therefore not included in the free energy the effect due to the mixing of isotopes nor the effect due to the nuclear spins which the isotopes may possess. Before proceeding further there is a point which will need special discussion. The Cl_2^{35-37} molecules have twice as many states as the Cl_2^{35-35} or Cl_2^{37-37} molecules and in considering the reaction $Cl_2^{35-35} + Cl_2^{37-37} = 2Cl_2^{35-37}$ we have recognized this fact in computing the $\Delta F/T$ given above. However, in calculating the equilibrium constant we have taken the standard state of each of the three kinds of molecules as that of unit fugacity. While

[8] Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

this was desirable for our investigation of the isotope effect, we wish to place the final calculations on the basis of a standard state which consists of the existing mixture of isotopic chlorine molecules in the ideal gas state at a total pressure of one atmosphere. This is in order to be consistent with ordinary thermodynamic procedure. In other words, we are going to agree to ignore the existence of isotopic molecules. Having done this we have imposed the requirement that we must not use any molecular quantum states which owe their origin to the presence of isotopes. We have in mind the fact mentioned above, that Cl_2^{35-37} has twice the number of rotational states possessed by the homopolar chlorine molecules. The Q obtained by summing over all states of the Cl_2^{35-37} molecule must be divided by 2 before computing the contribution which this molecule makes to the total Q of the mixture.

The necessity of the above procedure may be made clearer by considering the reactions

$$Cl_2^{35-35} = 2Cl^{35} \quad (a)$$
$$Cl_2^{35-37} = Cl^{35} + Cl^{37} \quad (b)$$
$$Cl_2^{37-37} = 2Cl^{37} \quad (c)$$

Neglecting the small effects due to the different masses it is evident that the equilibrium constant $K_a = K_c = 2K_b$, due to the double statistical weight of Cl_2^{35-37}. In this calculation the standard state of each gas is the ideal gas at unit pressure. However, although K_b is but one-half of K_a or K_c, it may be seen that the three chlorine molecules will dissociate to the same extent. If we consider a total pressure of Cl atoms amounting to one atmosphere in each case, the partial pressures of Cl^{35} and Cl^{37} in case b will be one-half atmosphere each. This factor of two just balances the double statistical weight of the Cl_2^{35-37} molecules. In other words, the increased entropy due to the double number of states in Cl_2^{35-37}, namely, $R \ln 2$, is just balanced by the entropy of mixing of the two different species of atoms resulting from its dissociation. Thus if the existence of the isotopic mixture is to be ignored, it is evident that the double weight of Cl_2^{35-37} must also be ignored. Similar consideration shows that in molecules which have a number of equivalent positions occupied by a given element, all statistical weight should be neglected which is created by the presence of two or more isotopes occupying otherwise equivalent positions.

It seems necessary to compare the self-consistent results of the above procedure with those obtained in the ordinary application of the third law of thermodynamics. We may state at once that they are consistent and may be combined with them. In fact, the above method of calculation is practically dictated by this consideration of convenience. As an example let us consider the Cl_2^{35-37} molecule in the solid state. The figure axis of the molecule will point in some direction specified by the crystal structure. However, the crystal will show no appreciable prefer-

ence as to which isotope is on a given end of the figure axis. This factor of two which is ignored by heat capacity measurements to the lowest available temperatures is just that which is concerned in the double statistical weight of the gas molecule which is to be ignored in our calculations. It has previously been pointed out[9] that in accordance with the third law, the positions of the various isotopes in the crystal become ordered so as to remove the uncertainty referred to above as the absolute zero is approached under equilibrium conditions. However, while this point is of theoretical interest in connection with the exact truth of the third law, it was also pointed out that the required conditions of sufficiently low temperature and attainment of equilibrium are not present in the ordinary application of this law.

The above considerations may be applied with the same results to more complicated molecules in the solid state.

There are, however, two respects in which we shall not ignore the isotope effect. First, the several isotopic molecules have slightly different molecular constants and the value of a given thermodynamic property for the substance as a whole will be obtained by adding the contributions of the several molecules, each in proportion to its abundance. Second, the double statistical weight of the Cl_2^{35-37} molecule is considered in obtaining the relative abundance of these molecules for computing the above average.

In this connection it is very interesting to compare the ordinary method of calculating abundance which assumes that each atom has equal chance with the method of observing the number of molecular states in determining the statistical weight of each kind of molecule. The chance of withdrawing two Cl^{35} atoms in succession from a mixture of the isotopic atoms is equal to $N^2_{Cl^{35}}$, where $N_{Cl^{35}}$ is its mole fraction. The chance of obtaining a Cl^{35} and a Cl^{37} atom in two successive draws is $2 \times N_{Cl^{35}} N_{Cl^{37}}$ since there is equal chance for each order of drawing Cl^{35}, Cl^{37} or Cl^{37}, Cl^{35}. When the statistical weight is calculated from the number of observed states of the molecules it is seen that the double weight of the Cl_2^{35-37} molecule compared to Cl_2^{35-35} is given by the double number of rotational states. Were it not for the fact that the nuclear spin of chlorine causes all of the energy levels to have some representatives, the Cl_2^{35-35} bands would have only one-half as many lines as the Cl_2^{35-37} bands. This phenomenon has been observed in the case of O_2^{16-16} and O_2^{16-18}.

In the case of chlorine the relative percentages of isotopes 35 and 37 are 75.9 and 24.1%, respectively. These values are obtained from the atomic weight 35.457 combined with the values 34.975 and 36.972 for the individual isotopes. These latter values were obtained from the work of Aston and are corrected on the basis of Mecke and Childs'[10] determination

[9] Giauque and Johnston, THIS JOURNAL, **50**, 3221 (1928).

[10] Mecke and Childs, *Z. Physik*, **68**, 362 (1931).

of the relative abundance of the oxygen isotopes. From the above figures it is found that chlorine gas is 57.6% Cl_2^{35-35}, 36.6% Cl_2^{35-37} and 5.8% Cl_2^{37-37}.

The values of $(F^\circ - E_0^\circ)/T$ are given in Table IV. As mentioned above, the value of $Q_{Cl_2^{35-37}}$ has been reduced by a factor of two.

The Free Energy of Hydrogen Chloride

The free energy of hydrogen chloride was calculated in the manner used for chlorine except that the summation method was used to 2000°K. This was done only for comparing the two methods of calculation as previously discussed.

The constants used for hydrogen chloride are those given by Kemble.[11] These have been expressed in terms of the more recent nomenclature and are collected in Table III.

TABLE III

CONSTANTS IN THE ENERGY EQUATION OF HCl^{35} IN Cm.$^{-1}$

$$B_v = 10.6080 - 0.3281(v + 1/2) + 0.01195(v + 1/2)^2$$
$$D_v = -0.000533 + 0.0000121(v + 1/2)$$
$$F_e = 1.46 \times 10^{-8}$$
$$\epsilon_v = 2994.33(v + 1/2) - 53.58(v + 1/2)^2$$

From the above data the free energy values for hydrogen chloride were calculated. As in the case of chlorine the effects of nuclear spin and isotopic mixing have been neglected but the free energies of the two isotopic molecules were calculated and have been given their proportionate weight in obtaining the final values. The free energy values for the two kinds of hydrogen chloride and the mixture are given in Table IV.

The Reaction $1/2\ H_2 + 1/2\ Cl_2 = HCl$.—We are now prepared to consider the reaction $1/2\ H_2 + 1/2\ Cl_2 = HCl$. Combining the free energy values for chlorine and hydrogen chloride given in Table IV with the free energy of hydrogen[1b] the $\Delta(F^\circ - E_0^\circ)/T$ for the above reaction is found. The $(F^\circ - E_0^\circ)/T$ values used for hydrogen are those obtained when the nuclear spin is ignored since this has also been done in the preparation of the present tables.

In Table V the values of $\Delta(F^\circ - E_0^\circ)/T$ are given along with values of $\Delta F^\circ/T$ and their resulting equilibrium constants.

In making these calculations the ΔE_0° used was obtained by combining the free energy of the reaction at 25° with the value of $\Delta(F^\circ - E_0^\circ)/T$ at this temperature. This free energy has been given by Randall and Young[12] as $\Delta F_{298.1} = -22{,}741$ calories. Since this value has been obtained from electromotive force measurements, the resulting value of $\Delta E_0^\circ = -21{,}984$ calories per mole is very reliable.

[11] Kemble, *J. Opt. Soc. Am.*, **12**, 1 (1926).

[12] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

The equilibrium constants given in Table V are not sufficient to give the extent to which hydrogen chloride will dissociate at high temperatures where the reaction is complicated by the dissociation of chlorine and of hydrogen. The dissociation constant for hydrogen has been previously given[1b] while that of chlorine may be calculated. For this we shall need the free energy of atomic chlorine which we shall now obtain.

The Free Energy of Atomic Chlorine.—The only electronic levels of the chlorine atom which need be considered for the present calculation are the $^2P_{1^1/_2}$ zero state and the $^2P_{1/_2}$ level which Kiess and DeBruin[13] have found to be 881 cm.$^{-1}$ above.

In Table V the values of $(F^\circ - E_0^\circ)/T$ are given for the isotopic mixture of atomic chlorine gas. As in the case of molecular chlorine and hydrogen chloride these values do not include the effect of nuclear spin or of isotopic mixing.

The Dissociation of Chlorine.—From the data in Table IV the $\Delta(F^\circ - E_0^\circ)/T$'s for the reaction $Cl_2 = 2Cl$ are obtained and given in Table V. These values, when combined with $\Delta E_0^\circ/T$, give $\Delta F^\circ/T$, which is also given in Table V.

The value of ΔE°_0 has been taken from Elliott's[6] revision of Kuhn's[14] determination of this quantity from the band spectrum of chlorine. The value 56,900 calories per mole is in good agreement with the value 57,000 given by Wohl and Kadow[15] on the basis of explosion experiments.

If the accepted value $\Delta E_0^\circ = 56{,}900$ calories per mole is altered by further investigation a very simple calculation will permit revision of the values given for $\Delta F^\circ/T$ and K in Table V.

Löwenstein[16] has measured the dissociation of hydrogen chloride by passing this gas through a platinum tube and observing the equilibrium pressure of hydrogen which diffused through the wall. His one observation at 1810°K. gave 0.274% dissociation. However, this value was calculated without making a correction for the dissociation of chlorine or of hydrogen. Löwenstein found an equilibrium pressure of 1.03 mm. of hydrogen when the total pressure was 751.2 mm. At 1810°K. and a total pressure of 1.03 mm. of hydrogen, the pressure of diatomic hydrogen is 1.018 mm. and that of atomic hydrogen 0.0115 mm., a very small correction. However, the error made by neglecting the dissociation of chlorine is more serious. Instead of 1.03 mm. pressure of Cl_2, calculation shows this pressure to be 0.044 mm. and the pressure of monatomic chlorine to be 1.96 mm.

From the above corrections to Löwenstein's values we calculate $K_{1810^\circ} = [HCl]/[H_2]^{1/2}\,[Cl_2]^{1/2} = 3.54 \times 10^3$, whereas by interpolation in Table IV

[13] Kiess and DeBruin, *Bur. Standards J. Res.*, **2**, 1117 (1929).

[14] Kuhn, *Z. Physik*, **39**, 77 (1926).

[15] Wohl and Kadow, *Z. physik. Chem.*, **118**, 460 (1925).

[16] Löwenstein, *ibid.*, **54**, 715 (1906).

TABLE IV

$(F^\circ - E_0^\circ)/T$ FOR CHLORINE AND HYDROGEN CHLORIDE GASES

	$-(F^\circ - E_0^\circ)/T$ calories per degree per mole							
T, °K.	Cl_2^{35-35}	$Cl_2^{35-37} - Cl_2^{35-35}$	$Cl_2^{37-37} - Cl_2^{35-35}$	Cl_2 equil. mixture	HCl^{35}	$HCl^{37} - HCl^{35}$	HCl mixture	Cl mixture
250	44.598	0.141	0.282	44.666	**36.447**	0.164	**36.487**	**33.555**
298.1	**45.881**	.144	.288	**45.951**	**37.695**	.164	**37.734**	**34.437**
300	**45.928**	.144	.288	**45.997**	**37.738**	.164	**37.778**	**34.468**
350	47.072	.146	.291	47.141	38.806	.164	38.847	**35.246**
400	48.078	.147	.294	48.148	**39.732**	.164	**39.771**	**35.924**
450	48.978	.148	.297	49.049	40.549	.164	40.589	**36.527**
500	**49.793**	.150	.299	**49.865**	**41.281**	.164	**41.321**	**37.070**
550	50.538	.150	.301	50.611	41.943	.164	41.983	**37.563**
600	51.225	.151	.303	51.298	42.548	.164	42.588	**38.015**
650	51.863	.152	.305	51.936	43.106	.164	43.146	**38.432**
700	**52.458**	.153	.306	**52.531**	43.623	.164	43.663	**38.820**
750	53.016	.153	.308	53.089	**44.106**	.164	**44.145**	**39.182**
800	53.540	.154	.309	53.614	44.557	.164	44.597	**39.521**
850	54.036	.155	.310	54.110	44.983	.164	45.023	**39.840**
900	54.506	.155	.311	54.580	45.385	.164	45.425	**40.141**
950	54.953	.156	.312	55.027	45.767	.164	45.807	**40.426**
1000	**55.378**	.156	.313	**55.453**	**46.131**	.164	**46.171**	**40.687**
1050	55.784	.157	.314	55.859	46.477	.164	46.517	**40.955**
1100	56.173	.157	.314	56.248	46.809	.164	46.849	**41.201**
1150	56.546	.157	.315	56.621	47.127	.164	47.167	**41.435**
1200	56.904	.158	.316	56.979	47.432	.164	47.472	**41.659**
1250	57.249	.158	.316	57.324	47.727	.164	47.766	**41.875**
1300	57.581	.158	.317	57.656	48.011	.164	48.051	**42.082**
1400	58.210	.159	.318	58.286	48.550	.164	48.590	**42.473**
1500	**58.800**	.159	.319	**58.876**	**49.056**	.164	**49.096**	**42.836**
1600	59.353	.160	.320	59.430	49.532	.164	49.572	**43.175**
1700	59.875	.160	.321	59.952	49.983	.164	50.023	**43.494**
1800	60.369	.161	.321	60.446	50.411	.164	50.451	**43.794**
1900	60.839	.161	.322	60.916	50.819	.164	50.859	**44.078**
2000	**61.285**	.161	.322	**61.363**	**51.208**	.164	**51.248**	**44.346**
2100	61.711	.161	.323	61.789	51.580	.164	51.619	**44.601**
2200	62.119	.162	.323	62.196	51.936	.165	51.976	**44.844**
2300	62.510	.162	.324	62.587	52.279	.165	52.319	**45.076**
2400	62.885	.162	.324	62.962	52.609	.165	52.649	**45.298**
2500	**63.246**	.162	.324	**63.324**	**52.928**	.165	**52.968**	**45.510**
2600	63.594	.162	.325	63.672	53.238	.165	53.276	**45.714**
2700	63.930	.162	.325	64.009	53.534	.165	53.573	**45.910**
2800	**64.256**	.163	.325	**64.334**	**53.820**	.165	**53.860**	**46.098**
2900	64.571	.163	.326	64.649	54.096	.165	54.137	**46.280**
3000	**64.878**	.163	.326	**64.956**	**54.364**	.165	**54.404**	**46.456**

The values given in heavy type are calculated by means of Equations 1 and 5b. The others were obtained by interpolating differences between the directly calculated $(F^\circ - E_0^\circ)/T$'s and approximate values calculated by assuming a constant moment of inertia and harmonic oscillation. The values obtained by combination of the interpolated differences with approximate values calculated for the intermediate temperatures gave results of practically the same reliability as those calculated directly.

TABLE V

FREE ENERGY CHANGES IN THE REACTION $^1/_2H_2 + {}^1/_2Cl_2 = HCl$ AND THE DISSOCIATION OF CHLORINE

	$^1/_2H_2 + {}^1/_2Cl_2 = HCl$			$Cl_2 = 2Cl$		
T, °K.	$-\Delta(F^\circ - E_0^\circ)/T$	$-(\Delta F^\circ/T)$	$K = [HCl]/[H_2]^{1/2}[Cl_2]^{1/2}$	$-\Delta(F^\circ - E_0^\circ)/T$	$\Delta F^\circ/T$	$K = [Cl]^2/Cl_2$
250	2.532	90.468		22.444	205.156	
298.1	2.541	76.288	4.730×10^{16}	22.923	167.953	1.95×10^{-37}
300	2.539	75.819		22.939	166.728	
350	2.511	65.322		23.351	139.220	
400	2.478	57.438		23.700	118.550	
450	2.442	51.295		24.005	102.439	
500	2.405	46.373	1.368×10^{10}	24.275	89.525	2.70×10^{-20}
550	2.367	42.338		24.515	78.940	
600	2.330	38.970		24.732	70.101	
650	2.293	36.115		24.928	62.610	
700	2.257	33.663		25.109	56.177	
750	2.221	31.533		25.275	50.592	
800	2.188	29.668		25.428	45.697	
850	2.156	28.020		25.570	41.371	
900	2.125	26.552		25.702	37.520	
950	2.095	25.236		25.825	34.070	
1000	2.068	24.052	1.808×10^{5}	25.941	30.959	1.71×10^{-7}
1050	2.041	22.978		26.051	28.139	
1100	2.016	22.001		26.154	25.573	
1150	1.992	21.109		26.249	23.229	
1200	1.968	20.288		26.339	21.078	
1250	1.947	19.534		26.426	19.094	
1300	1.928	18.839		26.508	17.261	
1400	1.890	17.593		26.660	13.983	
1500	1.855	16.511	4.064×10^{3}	26.796	11.137	3.68×10^{-3}
1600	1.822	15.562		26.920	8.643	
1700	1.792	14.724		27.036	6.435	
1800	1.766	13.979		27.142	4.469	
1900	1.744	13.315		27.240	2.707	
2000	1.723	12.715	6.015×10^{2}	27.329	1.121	5.69×10^{-1}
2100	1.704	12.173		27.413	−0.318	
2200	1.687	11.680		27.492	−1.628	
2300	1.668	11.226		27.565	−2.826	
2400	1.651	10.811		27.634	−3.926	
2500	1.633	10.427	1.902×10^{2}	27.696	−4.936	11.99
2600	1.616	10.071		27.756	−5.871	
2700	1.598	9.740		27.811	−6.737	
2800	1.582	9.433		27.862	−7.541	
2900	1.564	9.145		27.911	−8.290	
3000	1.546	8.874	8.702×10	27.956	−8.989	92.21

we find the reliable value $1.099 \times 10.^3$ The disagreement of the two values is very surprising. In order to bring agreement it would be necessary to assume a value for the heat of dissociation of chlorine which is about 15,000 cal./mole greater than the reliable one which we have used above.

It appears necessary to conclude that Löwenstein's single observation was subject to some very large error.

The Heat of Formation of Hydrogen Chloride.—From the equation[1a]

$$\Delta H^\circ = \Delta E_0^\circ + \Delta\left[\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right] = \Delta E_0^\circ + \Delta\left[\frac{5}{2}RT + N\frac{\Sigma\epsilon pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}\right] \quad (9)$$

A very reliable value for the heat of formation of gaseous hydrogen chloride from hydrogen and chlorine may be obtained. This calculation could be made for any temperature but we shall obtain only the value for $\Delta H^\circ_{298.1}$ which seems of the greatest utility.

For the equilibrium mixture of ortho and para hydrogen the value of $\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}$ is[1b] 2023.20 calories per mole at 298.1°K. For chlorine the value of $\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}$ = 2193.69 calories per mole at 298.1°K. This value was obtained by properly weighting the individual contributions of the three isotopic molecules as mentioned above. The effect of ortho and para states could be ignored in this calculation due to the essential establishment of the high temperature limiting equilibrium even at temperatures far below 298.1°K. The corresponding effect in hydrogen[1b] was only 0.01 calorie per mole at 298.1°K. For hydrogen chloride

$$\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} = 2064.30$$

Thus for the reaction $^1/_2H_2 + {}^1/_2Cl_2 = HCl$, $\Delta H = -21{,}984 - 44 = -22{,}028$ calories per mole. The only appreciable inaccuracy in this value is the same as that in the free energy change given by Randall and Young.[12] This is probably reliable to ±10 calories per mole.

It is of interest to note that both Thomsen and Berthelot found $\Delta H = -22{,}000$ calories per mole for the above reaction.

The Entropy of Hydrogen Chloride and of Chlorine.—From the equation

$$S = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P - 2.300 + R\ln Q + RT\frac{\mathrm{d}\ln Q^{1a}}{\mathrm{d}T} \quad (10)$$

the entropies of HCl^{35} and HCl^{37} were calculated.

At 298.1°K. and a pressure of one atmosphere HCl^{35}, $S_{298.1} = 44.619$ calories per degree per mole. HCl^{37}, $S_{298.1} = 44.783$ E. U. Thus for the existing mixture HCl, $S_{298.1} = 44.658$ E. U. This value does not include the entropy of isotopic mixing nor that due to nuclear spin. The value obtained for $S_{298.1}$, HCl from low temperature heat capacity measurements[17] is 44.5 E. U.

For chlorine Cl_2^{35-35}, $S_{298.1} = 53.235$ E. U.; Cl_2^{35-37}, $S_{298.1} = 53.389$ E. U. (one-half of states used on account of isotope effect); Cl_2^{37-37}, $S_{298.1} = 53.543$ E. U. Thus Cl_2, $S_{298.1} = 53.310$ E. U. This value may be compared with

[17] Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928).

one calculated by combining the temperature coefficient of the cell Ag + $^1/_2Cl_2$ = AgCl, determined by Gerke[18] with the entropies of silver chloride and silver obtained from the third law of thermodynamics. A very accurate value of the entropy of silver chloride has recently been made available through the work of Eastman and Milner[19] soon to be published. AgCl, $S_{298.1} = 22.97 \pm 0.07$ E. U. Combining this with a preliminary determination of the entropy of silver by P. F. Meads and one of us, that is, Ag, $S_{298.1} = 10.01$ E. U. and $\Delta S = -13.73$ E. U., $S_{298.1}$, Cl_2 is found to be 53.38 E. U., which compares very well with the spectroscopic value of 53.310 E. U.

In the above calculations we have gone into considerable detail in investigating the isotope effect. We have had in mind from the beginning that while the presentation of such an example was desirable, the main object was to eliminate the necessity of such detail in future calculations.

It is therefore suggested that in considering the thermodynamic properties of substances which consist of two or more isotopic molecules, the following procedure be adopted. Instead of using the several energy levels of the various isotopic molecules an average set of energy levels may be constructed by giving the proper weight to each isotopic molecule present. When the levels can be represented by equations, the above procedure requires only the computation of an average set of constants.

This procedure assumes that the isotopes have reached their limiting high temperature equilibrium. That this is reached with sufficient accuracy for calculations to 0.001 calorie per degree per mole, far below ordinary temperatures, has been demonstrated above.

Summary

An approximation method which permits the calculation of free energy from the energy levels of diatomic molecules without the necessity of summing the Boltzmann factors for the individual rotational energy levels has been given. The method considers the effects of molecular distortion due to rotation of the non-rigid molecules, without loss in accuracy.

The manner in which the presence of various isotopic molecules affects such calculations is discussed. It is shown that equilibrium in the reaction $Cl_2^{35-35} + Cl_2^{37-37} = 2Cl_2^{35-37}$ is entirely to the left at 0°K.

The values of $(F^\circ - E_0^\circ)/T$ for Cl_2^{35-35}, Cl_2^{35-37}, Cl_2^{37-37} and the equilibrium mixture have been tabulated for ready interpolation from 250°K. to 3000°K.

Similar tables have been prepared for HCl^{35}, HCl^{37} and for Cl^{35}, Cl^{37} and their respective existing mixtures.

The values of $\Delta F^\circ/T$ for the reaction $^1/_2H_2 + {}^1/_2Cl_2 = HCl$ have been

[18] Gerke, THIS JOURNAL, **44**, 1684 (1922).

[19] Personal communication.

presented so that values over the range 250 to 3000°K. may be easily obtained by interpolation.

The $\Delta F^\circ/T$ for $Cl_2 = 2Cl$ has been tabulated to 3000°K.

The change in heat content for the reaction $^1/_2H_2 + {}^1/_2Cl_2 = HCl$ has been accurately determined from the electromotive force of the hydrogen–chlorine cell and spectroscopic data. The value found was $\Delta H_{298.1} = -22{,}028$ calories per mole.

The entropies of hydrogen chloride and of chlorine have been calculated.

HCl^{35}, $S_{298.1} = 44.619$ E. U.
HCl^{37}, $S_{298.1} = 44.783$ E. U.
$HCl_{(mixture)}$, $S_{298.1} = 44.658$ E. U.
Cl_2^{35-35}, $S_{298.1} = 53.235$ E. U.
Cl_2^{35-37}, $S_{298.1} = 53.389$ E. U.
Cl_2^{37-37}, $S_{298.1} = 53.543$ E. U.
Cl_2 (equilibrium mixture), $S_{298.1} = 53.310$ E. U.

The entropy effect of nuclear spin (unknown for Cl^{37}) has purposely been omitted from the above values so that they may be used in combination with those obtained from low temperature heat capacity measurements. The entropy of mixing in the isotopic solutions and the entropy due to the presence of two isotopes in the same molecule have been eliminated for the same reason.

It is suggested that thermodynamic properties of substances which consist of two or more isotopic molecules be based on an average set of energy levels, computed by weighting the several values in proportion to the abundance of the respective molecules. The effect of the reduction in the number of levels by molecular symmetry on the above method has been discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

THE RATE OF SOLUTION OF ZINC IN ACIDS

BY CECIL V. KING AND M. M. BRAVERMAN

RECEIVED NOVEMBER 10, 1931 PUBLISHED MAY 7, 1932

The classical theory for the rate of solution of solids in aqueous solutions, developed by Noyes and Whitney,[1] Nernst[2] and Brunner,[3] postulates that the rate of chemical reaction in such cases is very high compared to the rate at which the active component of the solution can reach the solid surface by diffusion; hence the observed rate of dissolution will be that of diffusion to the surface through the products as they diffuse away.

[1] Noyes and Whitney, *Z. physik. Chem.*, **23**, 689 (1897).
[2] Nernst, *ibid.*, **47**, 52 (1904).
[3] Brunner, *ibid.*, **47**, 56 (1904).

This theory can by no means be as generally applicable to heterogeneous reactions as was supposed by the originators. We may assume with Van Name and Hill[4] that at least three types of heterogeneous reaction will be encountered: (1) the chemical reaction is very much faster than the diffusion rate, and the observed rate will be controlled by the latter; (2) the chemical reaction is very slow compared to the diffusion rate and the observed rate will be controlled by the former; (3) the diffusion rate constant and the reaction velocity constant are comparable in magnitude and the observed rate will be a function of both. In addition to these three types, many complications may appear, as "local elements" in the case of impure metals, solubility of the solid in pure water to an extent comparable to the concentration of the active component in the solution, formation of films at the surface by the reaction, etc.

In the case of metallic oxides, hydroxides and carbonates dissolving in acids, we should expect the chemical reaction to be so fast that the observed rate of solution would be controlled by the diffusion process. In the case of metals dissolving in acids, however, it is possible that the chemical reaction may be slower than the diffusion process. Experiments in such systems could be used advantageously in investigating the nature of acids by determining whether, as heretofore supposed, only the hydrogen ion reacts directly with the metal or whether other acid molecules or ions also enter directly in the reaction.

Brönsted, Lowry, Dawson and their co-workers have shown that in a number of homogeneous reactions not only the H_3O^+ and OH^- ions are active as catalysts, but also other acid and basic molecules. The chief criteria of such a catalysis are: (1) lack of proportionality of the rate to the hydrogen-ion concentration as one goes from strong to weak acids; (2) proportionality of the rate to the concentration of other acid molecules in solutions in which the hydrogen-ion concentration is buffered; (3) for an homologous series of acids, $\log k_A$ (rate constant) shows a linear relation to $\log K_A$ (acid dissociation constant).

The idea that undissociated acids may react with metals is not new; Kahlenberg and his co-workers carried out many experiments designed to show that this as well as other types of reaction can take place in the absence of ions. For example, Patten[5] found that $N/10$ hydrochloric acid in dry chloroform dissolves zinc faster than $N/10$ hydrochloric acid in water (until the reaction products choke the surface), in spite of the fact that the former solution has an exceedingly low electrical conductivity. However no attempt was made to show that other acids than the H_3O^+ ion react directly with metals in aqueous solution until Kilpatrick and Rushton,[6]

[4] Van Name and Hill, *Am. J. Sci.*, **42**, 307 (1916).

[5] Patten, *J. Phys. Chem.*, **7**, 153 (1903).

[6] Kilpatrick and Rushton, *ibid.*, **34**, 2180 (1930).

in a detailed study of the rate of solution of magnesium in monobasic acids,[7] applied the criteria of the above theory and showed that they were reasonably well fulfilled. The authors thus imply that the chemical reaction is much slower than the diffusion process and that they have measured the rate of the former. The mechanism is thus represented, for example in acetic acid, by the equations

$$Mg + 2H_3O^+ \longrightarrow Mg^{++} + 2H_2O + H_2$$
$$Mg + 2HAc \longrightarrow Mg^{++} + 2Ac^- + H_2$$

Brönsted and Kane have applied the same theory to the rate of solution of sodium from sodium amalgam by acids.[8] This reaction is complicated by the necessity of diffusion of sodium as well as of acid to the amalgam surface, and probably by adsorption of sodium in the amalgam surface.[9] The authors have, however, carefully considered the possible influence of diffusion on the observed solution rates; and conclude that this factor is all-important with the stronger acids, but that with acids of dissociation constant less than 10^{-7} the chemical reaction rates are sufficiently lower than the diffusion rates to be entirely responsible for the observed velocities.

Five observed facts have, in general, been accepted as criteria of the validity of the diffusion rate theory: (1) a number of different solids dissolve at nearly the same rate, while chemical reaction rates are seldom so nearly the same for such widely different substances; (2) the rate of stirring the solution or rotating the specimen has a very large influence on the observed rates, which is not typical of chemical processes; (3) the rate of solution is usually nearly inversely proportional to the viscosity of the solution; (4) the rates observed with different acids follow, in general, the diffusion coefficients of the acids rather than their acid strengths, although strict proportionality to diffusion coefficients obtained under entirely different experimental conditions cannot be expected; (5) the temperature coefficient of these heterogeneous reactions is usually 1.1 to 1.5 per 10° rise, while chemical reaction rates seldom have temperature coefficients less than 2. Neither Kilpatrick and Rushton nor Brönsted and Kane present experimental work to test the application of these five points in detail, and we feel that detailed study especially of (2), (3) and (5) will be necessary before their point of view can be accepted. Our own work shows that satisfactory formal agreement with the three criteria of the extended acid–base catalysis theory is not sufficient.

Experimental

For the experimental work presented here the rate of solution of zinc in acid solutions containing potassium nitrate as a depolarizer was chosen for

[7] Kilpatrick, *J. Chem. Ed.*, **8**, 1567 (1931).

[8] Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

[9] See Meyer, *Z. physik. Chem.*, **70**, 315 (1910), for the peculiar interfacial tension relation of sodium amalgam and solutions.

most of the experiments. It is to be expected that zinc will react chemically more slowly than the more active magnesium and sodium, although just how much effect an efficient depolarizer has on the inherent "activity" is problematical.

When hydrogen is allowed to form on the surface of the metal, undoubtedly the purity of the metal has considerable influence on the rate, especially for metals "whose solution tension is outweighed by the overvoltage of hydrogen."[10] It has been shown that many oxidizing agents greatly hasten the solution of such metals, especially when they eliminate hydrogen evolution entirely, even though they have no specific action on the metals themselves.[11] Potassium nitrate was chosen as a depolarizer, since it has no specific action, eliminates hydrogen evolution entirely, forms no insoluble coating on the surface of the metal, has little effect on the rate of solution of magnesium but increases that of zinc to nearly the same value as that of magnesium, and can be replaced by certain other depolarizers with almost identical results. Also it appears to reduce the effect of impurities in the zinc to a minimum.

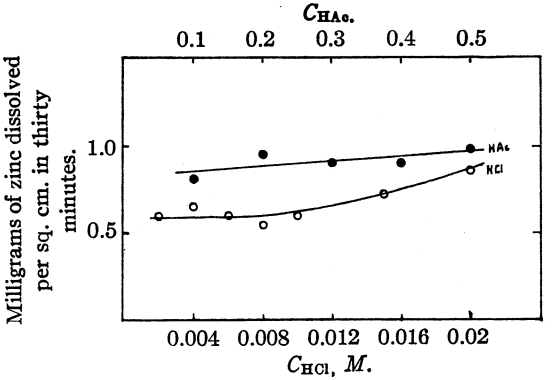


Fig. 1.—Rate of solution of zine in hydrochloric and acetic acids at 22°, 1600 r. p. m., no oxidizing agent.

Square plates, disks, or cylinders of the C. P. metal were attached to a bakelite shaft with bakelite nuts and rubber washers which prevented the solution from coming in contact with definite areas, in the case of the cylinders the entire end surfaces. Undoubtedly cylinders are most satisfactory for this type of experiment, since all points on the exposed surface will have the same linear speed through the solution; but the other specimens were satisfactory for the comparative experiments in which they were used. With the depolarizers present, there was no induction period and

[10] Centnerszwer, *Z. physik. Chem.*, **137A**, 352 (1928).

[11] Pullinger, *J. Chem. Soc.*, **57**, 815 (1890); Weeren, *Ber.*, **24**, 1785 (1891); Prins, *Proc. K. Akad. Amsterdam*, **23**, 1449 (1921).

the reactions were unimolecular, or nearly so. The loss in weight of the specimen during four or five minute intervals was taken as a measure of the rate constant; during this time the change in surface area was inappreciable and the decrease in acid concentration was only a few per cent. The volume of acid solution used and the temperatures are given with the tables and figures. The specimens were polished with fine emery paper before each run.

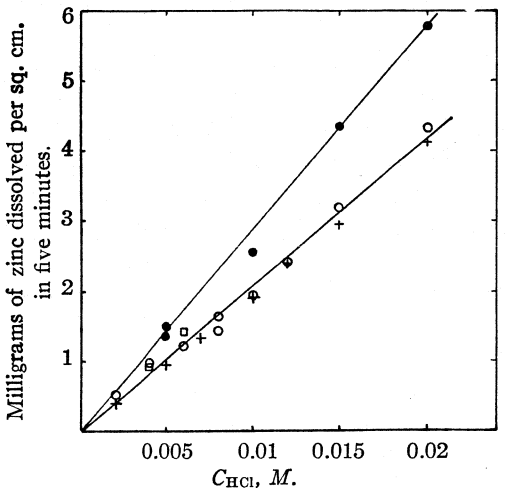


Fig. 2.—Rate of solution of zinc in hydrochloric acid at 23°: upper curve, 2800 r. p. m.; lower curve, 1600 r. p. m. ○, ●, 0.05 M KNO_3; □, 0.1 M KNO_3; +, 0.04 M H_2O_2.

1. Comparison of Different Acids.—Figure 1 shows the results obtained with hydrochloric and acetic acids with no oxidizing agents present. The rate of solution is nearly independent of the acid concentration and probably controlled by a nearly constant rate of hydrogen elimination. In a number of dilute acid and buffer solutions, with and without added inert salts, there was no significant dependence of this initial rate on the hydrogen-ion or total acid concentration. There is probably an induction period in such solutions and they have little quantitative significance.

Figure 2 summarizes the experiments with hydrochloric acid with added potassium nitrate and hydrogen peroxide, and compares the rate at two rotational speeds. The rate is, within experimental error, proportional to the acid concentration, independent of the particular oxidizing agent and its concentration (of course within limitations), and has little if any inert salt effect in the kinetic sense.

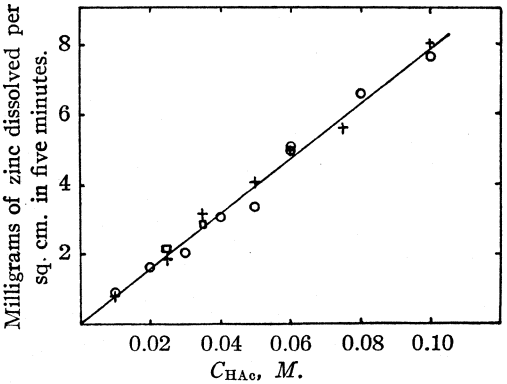


Fig. 3.—Rate of solution of zinc in acetic acid at 23°, 1600 r. p. m.: ○, 0.05 M KNO_3; □, 0.10 M KNO_3; +, 0.04 M H_2O_2.

In Fig. 3 are shown similar results for acetic acid. Again the rate is pro-

portional to the total acid concentration and not to the hydrogen-ion concentration; although the hydrogen ion of acetic acid accounts for some 10% of the total rate, the fact that its concentration was not controlled by using buffer solutions does not obscure the conclusions to be reached.

Figure 4 gives the results for formic acid at 1600 and 2800 r. p. m.; this change in rate of rotation increases the rate 38% with hydrochloric acid and 42% with formic acid. These values were used as a basis for estimating the constant at 2800 r. p. m. for acetic acid, as this was not measured directly.

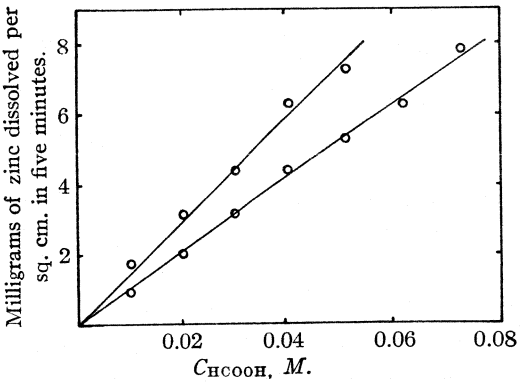


Fig. 4.—Rate of solution of zinc in formic acid at 25°, 0.05 M KNO_3 present; upper curve, 2800 r. p. m.; lower curve, 1600 r. p. m.

Figures 5 and 6 give measurements with glycolic, tartaric and citric acids. The latter two acids show practically the same rate, greater than the rate with hydrochloric acid at the same molar concentration.

Figure 7 summarizes measurements for boric acid and the ammonium ion (*i. e.*, solutions of ammonium chloride). The rates are very low, but fairly reproducible.

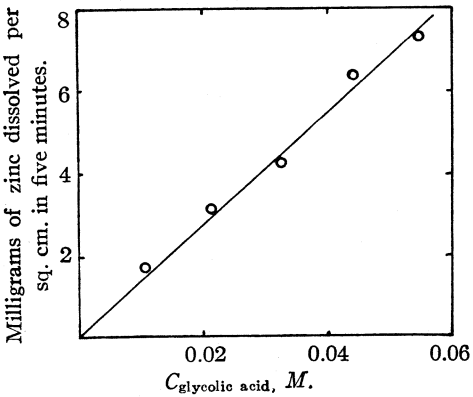


Fig. 5.—Rate of solution of zinc in glycolic acid at 23°, 2800 r. p. m.; 0.05 M KNO_3 present.

These rates are summarized in Table I and plotted in Fig. 8. The constants given have the dimensions of milligrams of zinc dissolved per square centimeter per five minutes per mole of acid per liter. The values have been calculated roughly for the undissociated acid present only, by assuming that hydrogen ion has the same effect per mole with all acids as with acetic acid (see Fig. 11). This is not strictly valid, but will serve our purpose here.

It is quite unlikely that we can attach any significance to the fact that on this log k_A–log K_A plot, the points, with the exception of the polybasic and very weak acids, lie near the straight line indicated. It seems more probable that the rates are determined largely by the diffusion rates, with

TABLE I

SUMMARY OF RATES OF SOLUTION OF ZINC IN ACIDS

3 × 3 cm. Squares of zinc rotated 2800 r. p. m. in 500 cc. of solution containing 0.05 *M* KNO_3, 23 ± 1°C.

Acid	k_A	Log k_A	Log k_A
H_3O^+	287	2.46	1.74
Tartaric	280	2.45	$\bar{3}$.04
Citric	290	2.46	$\bar{4}$.90
Formic	116	2.06	$\bar{4}$.32
Glycolic	112	2.09	$\bar{4}$.18
Acetic	97	1.99	$\bar{5}$.26
Mono-hydrogen citrate ion	123[a]	2.09	$\bar{6}$.51
Boric	2.0	0.30	$\overline{10}$.81
Ammonium ion	1.65	.22	$\overline{10}$.75

[a] Calculated from experiments with a cylinder at 4000 r. p. m.

the possible exception of those for boric acid and the ammonium ion. In these cases the low values may be due to the slowness of the chemical reaction or more likely to the formation of insoluble reaction products. The high rates with tartaric and citric acids are probably due to the fact that when the acid molecules reach the metal surface by diffusion they may furnish two and three hydrogen ions, respectively.

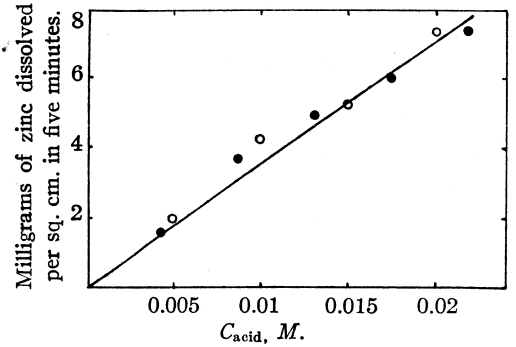


Fig. 6.—Rate of solution of zinc in citric and tartaric acids at 23°, 2800 r. p. m.; 0.05 *M* KNO_3 present: ●, citric acid; ○, tartaric acid.

2. Temperature Coefficients.—In Figs. 9 and 10 are shown the temperature coefficients, for hydrochloric and acetic acids. These were measured by rotating zinc disks 4 cm. in diameter, 2 mm. thick, clamped on a shaft with bakelite nuts and rubber washers 2 cm. in diameter, at a speed of 4000 r. p. m. The coefficients are: for acetic acid, $k_{25}/k_{15} = 1.28$ and $k_{35}/k_{25} = 1.26$; for hydrochloric acid, $k_{25}/k_{15} = 1.29$ and $k_{35}/k_{25} = 1.13$. The last value seems low and may be in error for some reason; our main point is to show that the values are typical of diffusion coefficients and much too low to be considered typical of chemical reaction rates.

3. Effect of a Common Ion with Acetic Acid.—Figure 11 shows the effect of adding comparatively small amounts of sodium acetate to acetic acid. Zinc disks rotating at 4800–5000 r. p. m. were used in these experiments. The effect is similar to that found by Kilpatrick and Rushton with magnesium. In the pure acetic acid we are measuring the rate due to the

combined diffusion of (1) dissociated acetic acid and (2) undissociated acid. In the presence of even 0.02 *M* sodium acetate, we are practically measuring the rate due to diffusion of undissociated acid alone, and further additions of the salt have a negligible effect. It will be noted that the portion of the rate due to the hydrogen ion (no sodium acetate present) is rather larger than would be expected if the chemical reaction rate were being measured (see Fig. 2). We have no way of deciding from these or any other of the experiments whether undissociated acetic acid or only hydrogen ion can actually react with the zinc. After some sodium acetate has been added, although dissociation is negligible so far as diffusion rates are concerned, the rate of dissociation is undoubtedly so high that all the acid could easily dissociate before reaction with no appreciable effect on the observed rate.

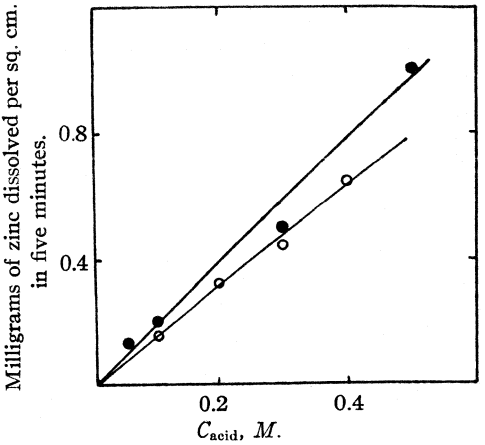


Fig. 7.—Rate of solution of zinc in boric acid and ammonium chloride at 23°, 1600 r. p. m., 0.05 *M* KNO_3 present: ●, boric acid: ○, ammonium chloride.

Figure 12 shows the effect of adding hydrochloric acid to a fixed amount of the acetic acid. The first addition of the strong acid represses the ionization of the weak one to a value negligible so far as diffusion rates are concerned; and with larger additions the rates are additive.

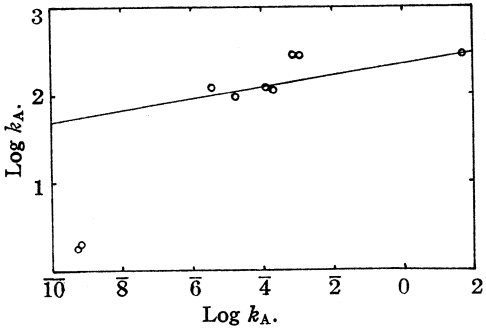


Fig. 8.—The data of Table I.

4. Effect of Rotational Speed.—The effect of increasing the speed of rotation of magnesium and zinc cylinders in hydrochloric and acetic acids is shown in Figs. 13 and 14. The rate increases apparently with some fractional power of the rotational speed (or perhaps better, the linear speed of the surface) up to about 1000 r. p. m.; above this point with the first power, or nearly so (in the case of zinc in hydrochloric acid), up to 5600 r. p. m. The rate has usually been found proportional to a fractional power of the rate of

stirring the solution or rotating the specimen, although in some cases the relation is linear;[12] but we have seen no results recorded at the higher speeds used here. The lack of any tendency for the curves to flatten must indicate that the observed solution rates are still controlled by the diffusion process. If we accept the Nernst picture of a "diffusion layer" surrounding the solid, the thickness of the layer can be calculated from the expression $k = D/\delta$ where k is the observed solution rate, D the diffusion coefficient, and δ the thickness of the layer. It is unlikely that the relation shown in Figs. 13 and 14 can continue until the diffusion layer becomes only a few molecules thick; but if the chemical reaction is not too fast it may be possible to attain such speeds that diffusion to the surface takes place more rapidly than the

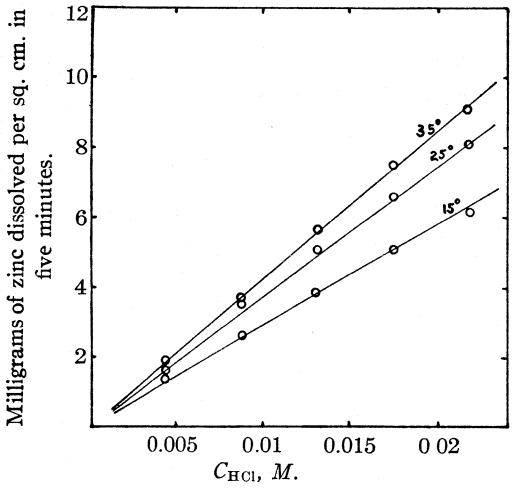


Fig. 9.—Temperature coefficient of rate of solution of zinc in hydrochloric acid, 0.05 M KNO_2 present, 4000 r. p. m.

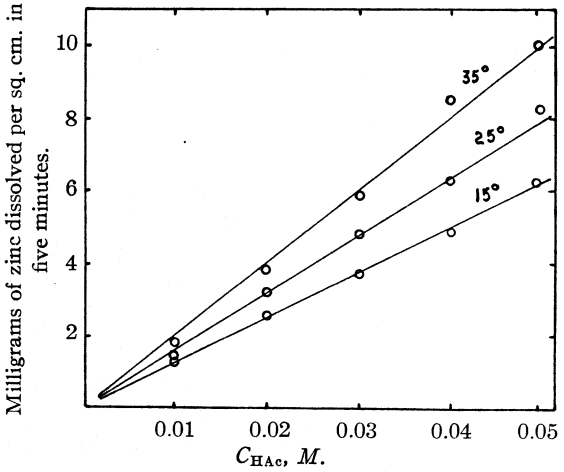


Fig. 10.—Temperature coefficient of rate of solution of zinc in acetic acid, 0.05 M KNO_3 present, 4000 r. p. m.

chemical reaction. However, frictional heating effects and other distur-

[12] Klein, *Z. anorg. allgem. Chem.*, **137**, 56 (1924).

bances apparently unimportant at 5600 r. p. m. with the cylinders used here, may become so at slightly higher speeds.

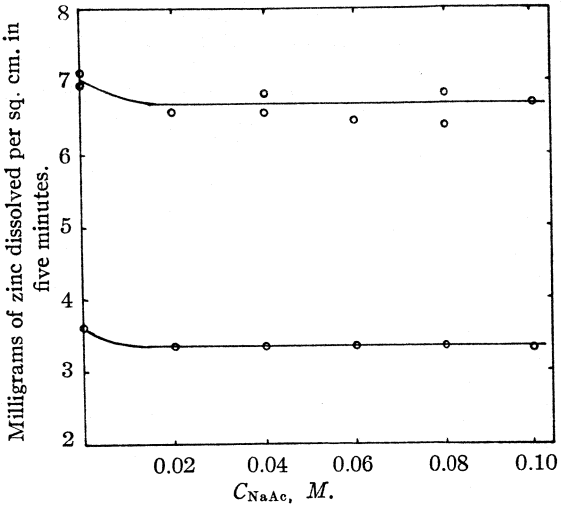


Fig. 11.—Effect of repressing the ionization of acetic acid (0.0122 and 0.0245 M) on its rate of dissolving zinc. 0.05 M KNO_3 present, 25–26°, 4800–5000 r. p. m., 500 cc. solution.

5. Effect of Viscosity Changes.—From the experimental relation between viscosity and diffusion rates $D\eta$ = constant, where η is the viscosity of the medium, and the relation $k = D/\delta$, it is seen that k will be inversely proportional to the viscosity, assuming δ to remain constant. Table II and Fig. 15 show the effect on the rate of solution of zinc obtained by changing the viscosity of a hydrochloric acid solution by adding cane sugar, alcohol and the salts listed. The viscosity values were taken from the

TABLE II

Rate of solution of zinc at 25° in 1000 cc. of 0.007 M HCl + 0.05 M KNO_3, 4000 r. p. m.; diameter of cylinder, 1.94 cm.

Additional solute	η_0/η	Mg. diss./sq. cm. in five min.
...	1	3.58
0.3 M sugar	0.71	2.68
.6 M sugar	.55	2.00
.9 M sugar	.38	1.45
1.2 M sugar	.27	0.94
1.5 M sugar	.17	.61
2.0 M NaCl	.80	2.81
2.0 M KCl	1.01	3.67
1.22 M $MgSO_4$	0.43	1.06
2.44 M $MgSO_4$	.17	0.39
24.7 vol. % C_2H_5OH	.49	1.73

Landolt-Börnstein "Tabellen," in the case of cane sugar by interpolation. The effect of 0.007 *M* hydrochloric acid and 0.05 *M* potassium nitrate on the viscosity was neglected.

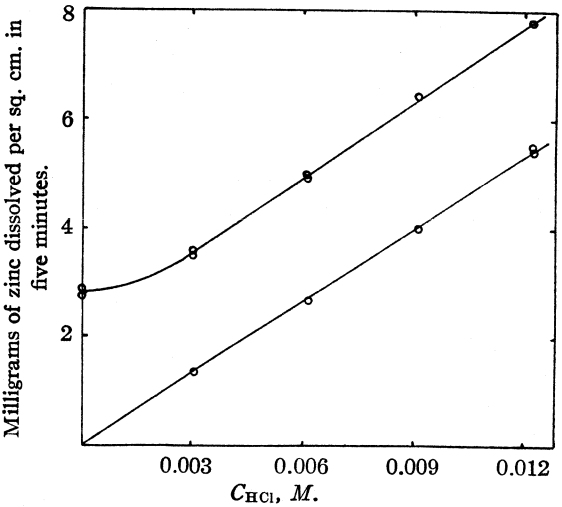


Fig. 12.—Rate of solution of zinc in mixed HCl and acetic acid: lower curve, HCl alone; upper curve, 0.0122 *M* acetic acid + HCl; 0.05 *M* KNO_3 present, 25-26°, 3800-4000 r. p. m., 500 cc. of solution.

That the inverse proportionality holds rather well is shown in Fig. 15. The results with magnesium sulfate may be in error because the solutions

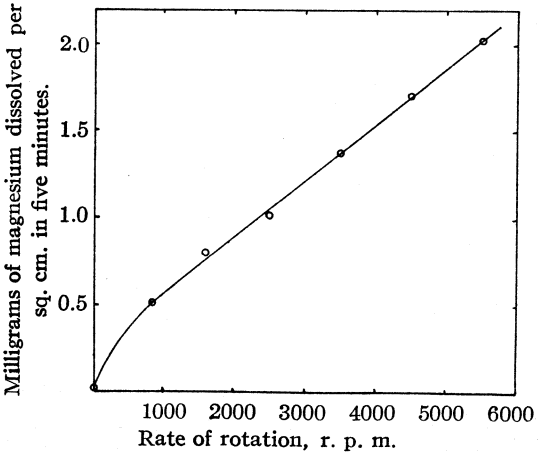


Fig. 13.—Effect of rotational velocity on rate of solution of a magnesium cylinder 2.16 cm. in diameter, 2.50 cm. long, in 0.0071 *M* HCl at 25°, 1 liter of solution.

were not made up very carefully; or possibly HSO_4^- ion may be formed in solutions of these high sulfate ion concentrations (?). The effect of salts is seen to be not a kinetic one, but merely due to the change in the viscosity of the solution.

Van Name and Hill[13] have measured the effect of alcohol up to 3 *M* and sugar up to 1 *M* on the rate of solution of cadmium in iodine–potassium iodide solutions. The results, when plotted as in Fig. 15, give a similar relation.[14]

Brönsted and Kane[8] mention the experiments of Zecchini[15] on the rate of solution of zinc in hydrochloric acid in a number of different solvents, and find it difficult to explain the rates as those of the chemical reaction. Zecchini's results are rather irregular but, considering the possible errors of the experiments, the rates, when plotted against $1/\eta$ for the pure solvents, do not fall unreasonably far from a straight line passing through the origin. Factors such as the solubility of zinc chloride and the overvoltage of hydrogen in the particular solvent must be important but, whatever the mechanism of the actual chemical reaction, the observed rates must be controlled largely by the diffusion process.

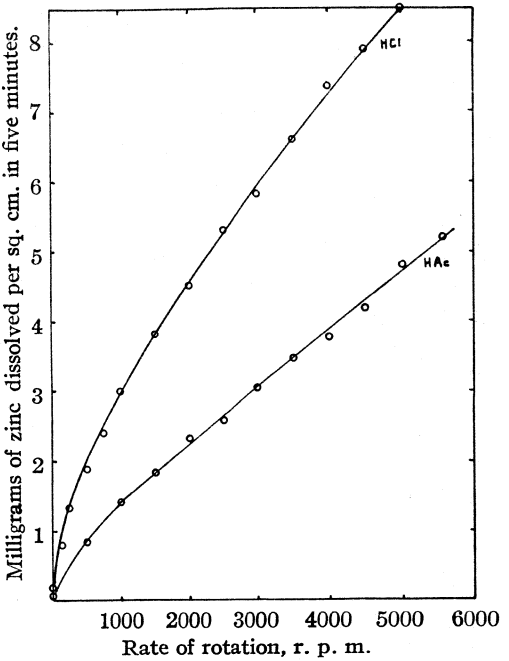


Fig. 14.—Effect of rotational velocity on rate of solution of a zinc cylinder 2.44 cm. in diameter, 1.88 cm. long, in 0.0142 *M* HCl and 0.0192 *M* acetic acid at 25°, 0.05 *M* KNO_3 present, 500 cc. of solution.

6. Comparison of Different Solids.—Magnesium, zinc and cadmium dissolve at far different rates in acid solutions containing no oxidizing agents, and the rate varies greatly with the purity of the metal. However, with potassium nitrate present, the rates are not widely different, and not far different from the rate of solution of marble. Table III gives quantitative results for these four substances.

[13] Van Name and Hill, *Am. J. Sci.*, [4] **36**, 543 (1913).

[14] The viscosities of sugar solutions given by Van Name and Hill are apparently somewhat in error.

[15] Zecchini, *Gazz. chim. ital.*, **27**, 466 (1897).

TABLE III

QUANTITATIVE RESULTS

Rates of solution at 25°, 1000 cc. of solution, 4000 r. p. m., 0.05 *M* KNO_3 used with Mg, Zn, Cd

	Diameter of cylinder, cm.	Milliequivalents of solid per cc.	Milliequivalents diss. per sq. cm. in 4 min.	
			0.007*M*HCl	0.03*M*HAc
Mg	1.91	145	0.094	0.124
Zn	1.95	220	.086	.128
Zn[a]	1.95	220	.080	.109
Cd	1.97	154	.076	.094
$CaCO_3$	1.87	540	.116	.134

[a] "Spectroscopically pure" zinc furnished by the New Jersey Zinc Co., to whom we wish to express our thanks.

It does not seem plausible that rates so nearly the same can be rates of chemical reaction for substances so widely different in chemical activity and in concentration. More probably the differences are due to differences in the solubility and diffusion rates of the reaction products and their effects on the diffusion rates of the acids. The higher values for marble in both acids might be explained by the disruptive effect of carbon dioxide bubbles on the "diffusion layer;"[16] but it is doubtful whether such bubbles were formed during four minutes of rotation in these solutions. Furthermore, the corresponding values for magnesium in similar solutions containing no potassium nitrate were: in 0.007 *M* HCl, 0.086 milliequivalent, somewhat lower than with nitrate present; in 0.03 *M* HAc, 0.134 milliequivalent, somewhat higher than with nitrate present. In this case the solutions became cloudy with very small hydrogen bubbles; their formation does not have a pronounced or consistent effect.

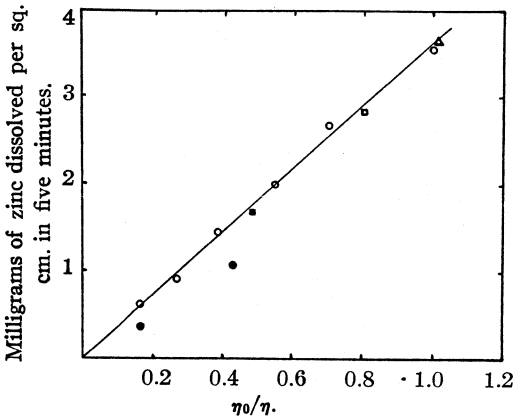


Fig. 15.—Dependence of the rate of solution of zinc in hydrochloric acid on the viscosity of the solution, 25°, 0.05 *M* KNO_3 present, 4000 r. p. m.: ○, sugar solutions; ●, 1.22 and 2.44 *M* $MgSO_4$; □, 2 *M* NaCl; ■, 24.7 volume % ethyl alcohol; △, 2 *M* KCl.

Van Name and Hill have proposed another explanation for small differences in the rate of solution of various metals in acid ferric chloride and ferric alum solutions.[17] If the rates of the chemical reactions are not very

[16] See Van Name and Hill, *Am. J. Sci.*, [4] **36**, 543 (1913).

[17] Van Name and Hill, *ibid.*, [4] **42**, 307 (1916).

much higher than the diffusion rates, they may have a noticeable effect on the solution velocities. The rates for marble, magnesium, zinc and cadmium are in the order one should expect if this explanation applies; but, if this were true, the differences would probably be more pronounced at this rotational speed.

A rough calculation from the experiments of Brönsted and Kane indicates that under the conditions described in Table III, 0.03 *M* $H_2PO_4^-$ ion would dissolve approximately 0.1 milliequivalent of sodium from an amalgam containing 0.14 milliequivalent per cc. (above which value the rate of solution is independent of the sodium concentration),[18] which suggests that this rate may likewise be controlled by the diffusion rate of the acid.

Summary

The rate of solution of zinc has been measured in a number of different acids. The simplification of the results obtained in the presence of certain oxidizing agents has been shown, the effect of acid concentration, rate of rotation and the temperature coefficient have been studied; and a comparison of the rate with those for other metals and marble has been made.

The results have been discussed from the viewpoints of the old "diffusion rate" theory and the Brönsted–Kilpatrick theory. While the former theory is not altogether satisfactory without modification, certain results are definitely contradictory to the latter.

It is impossible to decide at present whether other acids than the H_3O^+ ion react directly with magnesium, zinc, cadmium and marble, since previous experiments have measured rates controlled largely or entirely by diffusion rates.

NEW YORK, N. Y.

[18] Fraenkel and Heinz, *Z. anorg. allgem. Chem.*, **133**, 153 (1924).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

DIRECT MEASUREMENT OF THE PRIMARY, SECONDARY AND TOTAL MEDIUM EFFECTS OF ACETIC ACID

BY BENTON BROOKS OWEN

RECEIVED NOVEMBER 23, 1931 PUBLISHED MAY 7, 1932

Introduction

In calculating the "universal constant" in their equation for the activity coefficient of an electrolyte, Debye and Hückel[1] employ $D^{3/2}$, the $^3/_2$ power of the dielectric constant of the solvent. This satisfactorily describes the variation of activity coefficients with composition of the solvent so long as all activity coefficients are referred to unity at infinite dilution in their respective solvents. It is well known, however, that variation in solvent is also attended by an *absolute* change in the values of the activity coefficients (referring them all to one particular solvent), and that this absolute change is sometimes 10 to 100 times greater than the relative change accounted for by the term $D^{3/2}$ in the Debye–Hückel equation. In this paper these absolute and relative changes in activity coefficients, hereafter referred to as *primary and secondary medium effects*, will be given careful definition, and a number of fundamentally important equations concerning them will be derived. The direct calculation of the primary and total medium effects from e. m. f. data will be illustrated by the interesting case in which the medium itself, being a weak electrolyte in various concentrations, contributes to the ionic strength and complicates the calculations. The data were derived from cells containing hydrochloric acid, water, and acetic acid in various proportions, and from them a new empirical relation between medium effect and concentration of acetic acid will be derived, and compared with the relation discovered by Harned and Owen.[2]

Theoretical

The full generality and scope of the term medium effect was not apparent from the definition of Harned and Owen. They were concerned with the primary effect only, and, having found it proportional to the molality of acetic acid, referred to the proportionality constant as "the" medium effect. To secure the greatest generality, the emphasis must be removed from the proportionality constant and directed upon the influence of the medium on the activity coefficients, so that the definition may be free from any dependence upon empirical relationships.[3]

In a solution of an electrolyte in the presence of neutral (non-aqueous)

[1] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[2] Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

[3] It will be shown later that the proportionality found by Harned and Owen is probably approximate, even in dilute solution, and it was never considered valid for high concentrations.

molecules, the total medium effect is defined as the logarithm of the ratio of the activity coefficient of the electrolyte in the presence of the neutral molecules and in pure water at the same concentration of electrolyte. The primary medium effect is the limit to which the total effect converges as the electrolyte concentration approaches zero. The secondary medium effect is always given by the difference between the total and primary effects.

Throughout this paper all activity coefficients in any medium are referred to unity at infinite dilution in water, unless written with an asterisk (γ^*, y^*, etc.), in which case they are referred to infinite dilution in the medium itself. Subscripts indicate the electrolyte concentration, but will usually be omitted except in the important case where this is zero. When the medium is pure water, a superscript zero will be used; thus, $\gamma^0 = \gamma_m^0$, $\gamma_0^0 = 1$, etc. For all concentrations we may write

$$\log \gamma = \log \gamma_0 + \log \gamma^* \qquad (1)$$

and, by combining it with the identity

$$\log \gamma^0 \equiv \log \gamma_0^0 + \log \gamma^0 \qquad (2)$$

obtain a fundamental relation between total, primary and secondary medium effects, thus

$$\log \gamma/\gamma^0 = \log \gamma_0/\gamma_0^0 + \log \gamma^*/\gamma^0 \qquad (3)$$

For convenience the primary effect can be written simply $\log \gamma_0$ because $\gamma_0^0 \equiv 1$. Log γ^*/γ^0 is the secondary effect and in dilute solutions is calculable by

$$\log \gamma^*/\gamma^0 = -\alpha\sqrt{c} + \beta c \qquad (4)^4$$

where

$$\alpha = 352.6\,[(1/D)^{3/2} - (1/D^\circ)^{3/2}] \qquad (4a)^5$$

From the definition of total medium effect, it is obvious that its value may depend upon some or all of the following conditions: (1) nature and (2) concentration of the neutral molecules, (3) nature and (4) concentration of the electrolyte, and (5) the concentration units involved in the definitions of activity coefficient. The effect of varying all of these conditions (except the first) will be considered in this paper. Because Harned and Owen[2] have already discussed the primary medium effect of acetic acid in terms of "water-molality" units, it was decided to study conditions (2) and (5) simultaneously by making measurements and calculations in different units, and comparing the final results by suitable transformation formulas. Harned and Owen used "molality" for moles per kilo of water, but in the present paper, dealing with mixed solvents, the term "water-molality" is coined for this unit so that "molality" can retain its usual meaning—moles per kilo of solvent.

[4] It will be shown in a later section that equation 4 is quite accurate for concentrations as high as 0.2 normal; *cf.* Fig. 3.

[5] Using 0.357 for the universal constant at 25°, and $D^\circ = 78.8$; Noyes, THIS JOURNAL, **46**, 1098 (1924); Drude, *Ann. Physik*, **59**, 61 (1896).

Thus, for the double cell

$$\text{Ag-AgCl/HCl}_{(c)},\ \text{HAc}_{(C)}/\text{H}_2/\text{HCl}_{(c)}/\text{AgCl-Ag} \quad E^0 - E \tag{5}$$

the concentrations of hydrochloric acid and acetic acid are in moles per liter of solution. Using the letter "y" to represent activity coefficients when the concentrations are expressed in molarities, the e. m. f. is given at 25° by

$$E^0 - E = 0.05915 \log \frac{y_H y_{Cl} c_H c}{y_H^0 y_{Cl}^0 c^0 c^0} \tag{6}$$

Making $c = c^0$ to comply with the definition of medium effect, and writing y^2 for $y_H y_{Cl}$ and y^{02} for $y_H^0 y_{Cl}^0$, this equation becomes

$$(E^0 - E)/0.05915 - \log c_H/c = 2 \log y/y^0 \tag{7}$$

The term $\log c_H/c$ would, of course, be zero if the acetic acid were replaced by a non-electrolyte, but it will be shown that the ionization of acetic acid is sufficient to make this term amount to 3 to 10% of the total medium effect for the cells in which c is as low as 0.0296. Such values are, fortunately, still small enough to permit certain simplifying approximations in their calculation without introducing appreciable error into the corresponding medium effects. Their calculation will be taken up in some detail.

The ionization constant of acetic acid may be expressed in several concentration units. Thus, if $\overline{M}$ and C are (total) water-molality and molarity of acetic acid, and $\overline{m}$ and c are water-molality and molarity of hydrochloric acid, or the ions indicated by subscripts

$$K = \overline{\gamma}_A^2 \frac{\overline{m}_H \overline{m}_{Ac}}{\overline{M} - \overline{m}_{Ac}} = y_A^2 \frac{c_H c_{Ac}}{C - c_{Ac}} \tag{8}$$

and

$$C = \frac{\overline{M}(d - wc)}{1 + W\overline{M}}, \quad c = \frac{\overline{m}(d - wc)}{1 + W\overline{M}} \tag{9}$$

where d is the density of the solution, and w and W are the molecular weights in kilograms of hydrochloric and acetic acids, respectively. Writing the total acetic acid concentration for the concentration of un-ionized acetic acid, equation 8 may be combined with equation 9 to give

$$y_A^2 = \overline{\gamma}_A^2 (1 + W\overline{M})/(d - wc) \tag{10}$$

and

$$c_H = c + KC/(c_H y_A^2) \tag{11}$$

Equation 11 yields c_H if y_A^2 is known; but y_A^2 depends upon the medium effect being sought. Fortunately, if the assumption[6] be made that $\overline{\gamma}_A$ is approximately the same in HCl–HAc and NaCl–HAc solutions of equal ionic strength and HAc concentration, $\overline{\gamma}_A$ (and hence y_A) may be estimated

[6] This assumption can reasonably be expected to give values of $\overline{\gamma}_A$ less than 10 to 15% in error when c is as low as 0.0296, and such an accuracy is more than is required for this lowest concentration studied. For higher concentrations the error that can be tolerated in $\overline{\gamma}_A$ increases very rapidly with the concentration, as a glance at equations 7 and 11 will show.

from the curves and data published by Harned and Owen. Thus, the empirical equation[7]

$$\log \overline{\gamma}_A^2 = -\sqrt{\mu} + (0.75 + 0.055\,\overline{M})\,\mu \qquad (12)$$

allows the calculation of values of $\log \overline{\gamma}_A^2$ differing from the observed experimental values by less than 5% so long as $\overline{M}$ does not exceed 10, or μ exceed 0.3.

Experimental

The acids used were of the highest purity obtainable commercially. The freezing point of the acetic acid indicated 0.1% water by comparison with the tables of Rudorff.[8] All solutions were made up by weight (corrected for displaced air) in accurately gaged 500-cc. flasks, and every effort was made to have all concentrations known to better than 0.1%. Fresh electrodes were prepared for each cell from silver oxide[9] and pure chloroplatinic acid.[10] The cells were the simple H-type. Vacuum technique was not employed in filling them because the acetic acid cells and reference cells were prepared and measured identically, and only the *difference* in their e. m. f.'s enters into medium effect calculations. The hydrogen was electrolytic from sodium hydroxide solution. The cells attained equilibrium in two to four hours, after which their potentials were constant within a few hundredths of a millivolt. The recorded potential is the average of readings taken over two or three hours at equilibrium, and corrected to a partial pressure of one atmosphere of hydrogen. To make these corrections, the excess of each solution not required for filling cells was used for vapor pressure measurements in a 200-cc. isoteniscope. Contrary to the results of earlier investigators,[11] who found vapor pressures of the order of 30 mm. for 20 to 75% acetic acid solutions, the results of these measurements were in rough agreement with Raoult's law. The general form of the vapor pressure–composition curves can be represented by the data in Table I to better than the nearest mm. of mercury.

Table II records the experimental data and various calculated functions. To express the concentration of acetic acid, its mole fraction in the solvent

[7] The family of curves A to F in Fig. 1 of Harned and Owen's paper may be represented by straight lines

$$(\log k' - \sqrt{\mu'}) = \log k^0 - 0.75 + (0.055\,\overline{M})\,\mu'$$

for small ionic strengths. Their slopes were read from a large plot and found to be a complicated function of $\overline{M}$, which could, however, be simplified to $0.75 + 0.055\,\overline{M}$ as a first approximation. Equation 12 is derived by combining this equation with $\log k^0/K = \log k'/k$ (equation 17, Harned and Owen) and $\log K = \log \overline{\gamma}_A^2 + \log k$ (definitional), and remembering that μ' is not very different from μ in HCl–HAc solutions.

[8] Rudorff, *Ber.*, **3**, 390 (1870).

[9] Electrode Type 2, Harned, THIS JOURNAL, **51**, 416 (1929).

[10] Harned, *ibid.*, **48**, 326 (1926).

[11] Kahlbaum, *Z. physik. Chem.*, **13**, 51 (1894); Konowalow, *Wied. Ann.*, **14**, 34 (1881).

TABLE I

VAPOR PRESSURES OF HCl–HAc–H_2O SOLUTIONS AT 25°

Solvent, % HAc.....	15%	35%	60%
	Vapor pressures in mm.		
Molarity of HCl = 1.116	21.5	21.0	19.5
Molarity of HCl = 0.03 to 0.56	22.0	22.0	21.0

(N, Column 1) was selected because of the straight line relation exhibited in Fig. 1. In Column 3 are recorded the e. m. f. data for the half-cells comprising equation 5. The first e. m. f. in each section of the table is for a

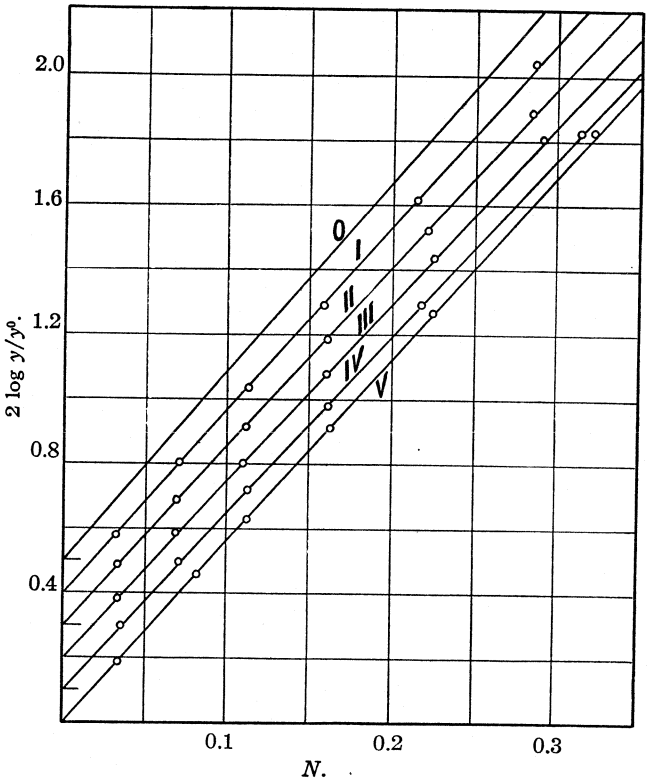


Fig. 1.—Variation of total medium effect with mole fraction of acetic acid. The origins of the five uppermost curves have been shifted. Normality of hydrochloric acid—0; I = 0.0296; II = 0.1112; III = 0.2255; IV = 0.5655; V = 1.1160.

cell containing c-molar hydrochloric acid, but no acetic acid. It is therefore E^0, the e. m. f. of the reference cell, for that particular section. Of course, c is constant throughout each section and is identical to c_H for the reference cell heading the section. Each e. m. f. is the average for two similar cells, except the reference values, which are each the average for

four cells. The difference between any two e. m. f.'s averaged is given as δE in millivolts. When four e. m. f.'s are averaged, δE is the greatest difference between any two. The values of $\bar{\gamma}_A^2$ were calculated by equation 12, c_H by equation 11, and 2 log y/y^0 by equation 7. The densities, d, are included to make possible the transformation of N and c into other concentration units. The quantities NJ in the last column are given to demonstrate the extent of the validity of the empirical equation 13, the values of J being given in parentheses at the top of each section.

TABLE II

DATA ON CELLS CONTAINING HYDROCHLORIC ACID IN ACETIC ACID–WATER SOLUTIONS AT 25°

N	d	$\frac{E}{0.05915}$	δE	$\bar{\gamma}_A^2$	c_H	Log (c_H/c)	2 Log y/y^0	NJ
0.0	0.9975	6.9478	0.04	..	0.02960	0.0	0.0	(5.669)
.0319	1.0110	6.7526	.01	0.709	.03081	.0174	.1778	.1808
.0705	1.0244	6.5158	.09	.712	.03177	.0307	.4013	.3997
.1124	1.0354	6.2773	.0	.719	.03239	.0391	.6314	.6372
.1583	1.0445	6.0154	.01	.728	.03275	.0439	.8885	.8974
.2147	1.0523	5.6856	.19	.744	.03288	.0456	1.2166	1.2171
.2861	1.0589	5.2651	.09	.764	.03278	.0443	1.6384	1.6221
0.0	0.9990	5.8681	.04	..	.11120	0.0	0.0	(5.542)
.0329	1.0129	5.6831	.15	.577	.11162	.0016	.1834	.1823
.0692	1.0252	5.4810	.0	.595	.11193	.0029	.3842	.3835
.1115	1.0364	5.2517	.05	.604	.11216	.0037	.6127	.6179
.1604	1.0460	4.9798	.10	.653	.11223	.0040	.8843	.8889
.2210	1.0542	4.6429	.08	.702	.11222	.0040	1.2212	1.2248
.2843	1.0598	4.2770	.09	.768	.11212	.0036	1.5875	1.5756
0.0	1.0010	5.2822	.10	..	.22550	0.0	0.0	(5.486)
.0329	1.0145	5.1012	.01	.521	.22573	.0004	.1806	.1805
.0688	1.0270	4.9008	.16	.556	.22588	.0007	.3807	.3774
.1100	1.0378	4.6813	.02	.602	.22597	.0009	.6000	.6035
.1605	1.0477	4.4035	.10	.670	.22600	.0010	.8777	.8805
.2253	1.0564	4.0477	...	.786	.22595	.0009	1.2336	1.2360
.2914	1.0623	3.6773	.19	.951	.22587	.0007	1.6042	1.5986
0.0	1.0072	4.4784	.08	..	.56550	0.0	0.0	(5.483)
.0351	1.0215	4.2827	.04	.540	.56559	.0001	.1956	.1925
.0704	1.0330	4.0870	.10	.647	.56563	.0001	.3913	.3860
.1128	1.0440	3.8608	.13	.775	.56565	.0001	.6175	.6185
.1616	1.0535	3.5999	.07	1.01	.56563	.0001	.8784	.8861
.2178	1.0610	3.2872	.0	1.42	.56560	.0001	1.1911	1.1942
.3143	1.0690	2.7513	.06	2.90	.56555	.0001	1.7270	1.7233
0.0	1.0166	3.8015	.11	..	1.1160	0.0	0.0	(5.631)
.0331	1.0300	3.6173	.13	..	1.1160	.0	.1842	.1864
.0817	1.0447	3.3441	.01	..	1.1160	.0	.4574	.4601
.1127	1.0527	3.1722	.15	..	1.1160	.0	.6293	.6346
.1622	1.0620	2.8911	.32	..	1.1160	.0	.9104	.9140
.2244	1.0699	2.5367	.02	..	1.1160	.0	1.2648	1.2636
.3224	1.0773	1.9739	.11	..	1.1160	.0	1.8276	1.8155

Discussion of Results

The family of straight lines obtained by plotting the medium effect against the mole fraction of acetic acid in the solvent is illustrated in Fig. 1, and represented mathematically by

$$2 \log y/y^0 = NJ \tag{13}$$

J is independent of N, but varies with c after the manner of an activity coefficient. The important primary medium effect is equal to the total medium effect at infinite dilution of electrolyte, and can therefore be obtained by extrapolation of $2 \log y/y^0$, or its equivalent NJ. Since $y_0^0 \equiv 1$, equation 13 becomes

$$2 \log y_0 = NJ_0 \tag{14}$$

at infinite dilution, and $\log y_0$ is the primary medium effect. The form of the extrapolation function can be derived by combining equations 3 and 4, transposing, and rewriting in the proper concentration units, thus

$$(2 \log y/y^0 + 2\alpha \sqrt{c}) = 2 \log y_0 + 2\beta c \tag{15}$$

The parameter α varies with N and could be calculated by equation 4a if the dielectric constant of the medium were known. Unfortunately, this is

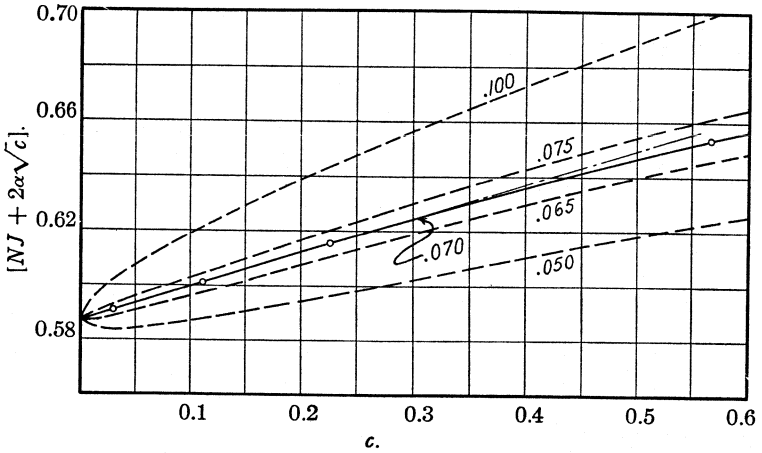


Fig. 2.—Extrapolation to J_0 for the various values of α as indicated, and $N = 0.1$.

not known, but the value of α, giving a straight line (in dilute solution, at least) when the terms in parenthesis are plotted against c, can be determined by trial. In Fig. 2, equation 15 has been plotted for $N = 0.1$ and the several values of α indicated. A straight line is obtained in dilute solution when $\alpha = 0.07$, and it extrapolates to $J_0 = 5.87$. Such a value of α would demand that the dielectric constant of 27% acetic acid solution (mole fraction 0.1) be about 72, which is not unreasonable, but as long as there is no experimental check on this value, α should be regarded as

purely empirical, for it is quite possible that the dielectric constant is much lower and the curvature of the uppermost curves is due to suppression of the "ionic radius" term of the Debye–Hückel formula used in deriving equation 4a.

The secondary medium effect has been defined as the difference between the total and primary medium effects. Since these latter have been shown to be proportional to N (Equations 13, 14), it follows that the *secondary medium effect*, *log* y^*/y^0, must also be proportional to N; thus, c being constant

$$\log y^*/y^0 = {}^1/_2N(J - J_0) \qquad (16)$$

In dilute solutions, the variation of the secondary medium effect with the concentration of electrolyte, is given by equation 4 rewritten in the proper units, thus, N being constant

$$\log y^*/y^0 = -\alpha\sqrt{c} + \beta c \qquad (17)$$

In Fig. 3 the experimental values of log θ, calculated for $N = 0.1$ by equation 16, are indicated by points on the continuous curve. The dashed

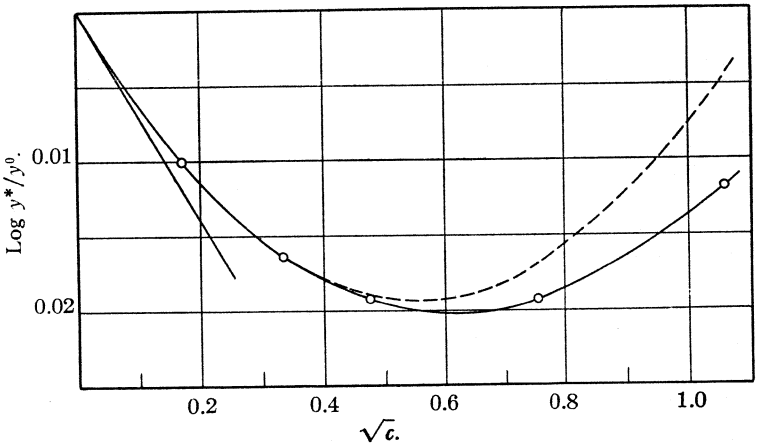


Fig. 3.—Variation of secondary medium effect, N being constant and equal to 0.1: —○—, ${}^1/_2 N (J_0 - J)$; – – –, $0.07 - \sqrt{c} + 0.063c$.

curve represents the values calculated by equation 17, using the values $\alpha = 0.07$ and $\beta = 0.063$ corresponding to the straight line (slope $= 2\beta$) in Fig. 2. These curves demonstrate that equations 4 and 17 fit the experimental data quite accurately up to $c = 0.2$.

Complete weight and density data were recorded in making up the cell solutions, so that a study could be made of the effect of different concentration units in plotting the medium effect, in the hope of discovering other relations similar to equations 13 and 14. No other simple relationship was found, although combinations of water-molality, molality and molarity were tried, but the relation of Harned and Owen (equation 17, their paper)

should be derivable from these data if differences in calculation and definition of medium effect be taken into consideration. This involved making the ionic strength (c_H) identical on both sides of the cell (equation 5), thus changing both the value of E^0 and the sign of log c_H/c in equation 7. The net result of these changes was a series of medium effects almost identical with those calculated by equation 7.[12] The transformation of all of these medium effects into water-molality units proved to be a very complicated proceeding and involved so many graphical interpolations that it was abandoned in view of the fact that transformation of units could not be expected to improve extrapolation by equation 15. The primary medium effect, however, may be studied much more directly.

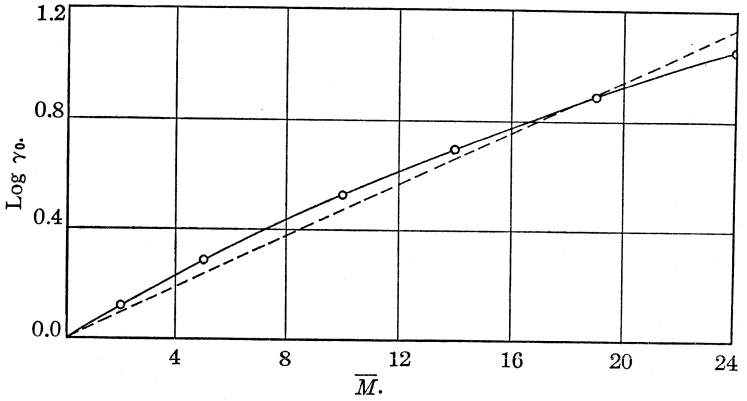


Fig. 4.—Variation of primary medium effect of acetic acid with molality. Broken line from calculations of Harned and Owen.

The primary medium effects in different concentration units are simply interrelated at *zero ionic strength.*

$$\log y_0 = \log \gamma_0 + \log d^0/d = \log \overline{\gamma}_0 + \log d^0/d + \log (1 + W\overline{M}) \qquad (18)$$

γ_0 corresponds to m in moles per kilogram of solvent, $\overline{M}$ is the water-molality of the non-aqueous component of the solvent, and W is its molecular weight in kilograms. The density of water, d^0, appears because the standard state of y_0 is 1000 cc. of pure water, and not 1000 g., as for $\overline{\gamma}_0$ and γ_0. This equation is general, being derivable from definitions only. Thus, at infinite dilution of electrolyte, $a_0 = m_0\gamma_0 = \overline{m}_0\overline{\gamma}_0 = c_0y_0(1/d^0)$ and $c_0 = m_0d = \overline{m}_0d/(1 + W\overline{M})$ (*cf.* equation 9), which give equation 18 by simple combination. Using $J_0 = 5.87$ in equation 14, and combining it with equation 18, log γ_0 and log $\overline{\gamma}_0$ may be calculated for any value of N for which equation 14 is valid (up to about $N = 0.25$). In Fig. 4, log $\overline{\gamma}_0$ calculated in this way is plotted with the straight line obtained by Harned

[12] All values were identical with those in Column 8, Table II, except those for c = 0.0296 and 0.1112, which were slightly higher, J being 5.695 and 5.545, respectively.

and Owen.[13] It will be observed that the numerical agreement is fair, considering the differences involved in the methods of calculation and their complexity, but the form of the two curves brings out the fact that $2 \log y_0 = NJ_0$ and $2 \log \bar{\gamma}_0 = \overline{M}S$ are not compatible. This means that one, or perhaps both, of these relations is not strictly true, but this is not surprising because they are both empirical and deal with fairly concentrated solutions of acetic acid. Furthermore, Harned and Owen's relation could not be expected to hold for very concentrated solutions because it would lead to the absurd result that the activity coefficient of hydrochloric acid is infinite in pure acetic acid.

The results of Åkerlöf's[14] study of hydrochloric acid and the alkali chlorides, in water–methyl alcohol solutions, not only permit the verification of two important equations interrelating the medium effects in terms of different electrolytes, but also can be used to demonstrate the general applicability of equation 15 in the calculation of primary medium effects. In his paper the electrolyte concentrations are expressed in moles per kilogram of solvent, and the composition of the solvent is expressed in per cent. of methyl alcohol by weight. In such units no simplifying relation corresponding to equation 13 is evident, so the determination of the primary medium effect, $\log \gamma_0$ (written $\log \gamma_\infty$ in his notation), necessitated an extrapolation for each concentration of methyl alcohol studied. Equation 15 is readily adapted to this purpose. If E' be the total e. m. f. of the amalgam double cells used by Åkerlöf, or the total e. m. f. $(E^0 - E)$, of a hydrochloric acid double cell (similar to equation 5, if the acetic acid be replaced by methyl alcohol, and c by m), then the total medium effect is given by[15]

$$E' = (0.05915)\, 2 \log \gamma/\gamma^0 \qquad (19)$$

Combining this equation with equation 15, expressed in appropriate units, and writing α' for $0.05915\ \alpha$ and β' for $0.05915\ \beta$, we obtain a very useful and simple extrapolation function,

$$(E' + 2\alpha'\sqrt{m}) = 0.1183 \log \gamma_0 + 2\beta' m \qquad (20)$$

Extrapolation of Åkerlöf's data by this equation leads to two significant results. In the case of hydrochloric acid, the extrapolation is very nearly a straight line when α' is calculated from the known dielectric constants by equation 4a, and the extrapolated values of $\log \gamma_0$ agree closely with $\log \gamma_\infty$ calculated by Åkerlöf. In the case of the alkali chlorides, these theoretical values of α' appear to be too small, for the extrapolation function bends upward as the axis is approached, much after the manner of the

[13] From their paper (equation 17), $S\overline{M} = 2 \log \bar{\gamma}_{HCl}/\bar{\gamma}^0_{HCl}$, which becomes $S\overline{M} = 2 \log \bar{\gamma}_0$ in the present nomenclature at zero ionic strength. Their value of S is 0.047.

[14] Åkerlöf, THIS JOURNAL, **52**, 2353 (1930).

[15] *Cf.* equation 7. The ionization of methyl alcohol is negligible compared with that of the chlorides, or hydrochloric acid.

lowermost curves in Fig. 2. This behavior is in accord with Åkerlöf's findings, for he was unable to fit his data to the Debye–Hückel equation without arbitrarily assigning greater values to the "universal constant" than those calculable from the dielectric constants.

Medium Effect on Different Electrolytes.—Two approximate equations interrelating the primary medium effects of a given solvent upon two similar electrolytes may be derived immediately from equation 20, and applied to Åkerlöf's data[14] to obtain an idea of the concentration range throughout which they may be safely used. Writing equation 20 for each of two electrolytes of the same concentration and medium and subtracting one equation from the other, we obtain an equation in which m appears only in the term $2m(\beta'_{(1)}-\beta'_{(2)})$, which may be neglected when m is small, and we may write

$$E'_{(1)} - E'_{(2)} = 0.1183 (\log \gamma_{0(1)} - \log \gamma_{0(2)}) \qquad (21)$$

Åkerlöf's data show that the approximation involved in the use of this equation for concentrations as high as 0.05 in 50% alcohol correspond to an experimental error of 0.2 to 0.3 millivolt.

Rewriting equation 20 for two electrolytes of the same concentration and medium and dividing the two equations one by the other, we obtain two ratios, each containing terms in m. Fortunately, the m-terms appear only as additions to larger terms, and are therefore negligible by comparison when m is small, and the ratios may be simply written

$$\frac{E'_{(1)}}{E'_{(2)}} = \frac{\log \gamma_{0(1)}}{\log \gamma_{0(2)}} = R_{(1,2)} \qquad (22)$$

This equation has been tested for all possible combinations of the three alkali chlorides and hydrochloric acid up to $m = 0.5$ and 50% alcohol, and found to describe the data with an average uncertainty of about plus or minus 6%, and individual deviations sometimes twice this figure. Such a high uncertainty[16] is unfortunate, but does not prevent the equation from rendering very important service where complete data are lacking, for *within the same limits of accuracy* $R_{(1,2)}$ *is independent of both m and the alcohol concentration.* Thus, if complete medium effect data are available for electrolyte (1), only one additional measurement, $E'_{(2)}$, is required for the approximate calculation of complete medium effect data for a similar electrolyte (2) within the limits of concentration and accuracy just specified.

Summary

1. The primary, secondary and total medium effects have been clearly defined, and equations presented for their calculation from electromotive force data.

2. Electromotive force measurements have been made upon hydrochloric acid solutions containing acetic acid. From these data the total

[16] Due in part to a mathematical magnification of experimental errors.

medium effect of acetic acid has been directly determined, and full details of the calculations are included.

3. A simple extrapolation function has been derived, and applied to a determination of the primary medium effect of acetic acid and to the data of Åkerlöf.[14]

4. It has been demonstrated experimentally that the primary, secondary, and total medium effects of acetic acid are closely proportional to the mole fraction of acetic acid in the solvent when the concentration of the electrolyte is expressed as molarity.

5. Equations relating the primary medium effects in different concentration units were derived and applied to a comparison of the primary medium effect obtained in this paper, with that calculated by Harned and Owen[2] from data on sodium chloride solutions containing acetic acid.

6. Two useful approximate equations were derived which interrelated the primary medium effects of a particular medium upon two similar electrolytes. The importance of these equations, in the calculation of approximate medium effects from very limited data, has been pointed out, and the magnitude of the approximations involved has been estimated from Åkerlöf's data.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL SCHOOL OF THE UNIVERSITY OF MELBOURNE]

THE SPEED OF DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF HYDROCHLORIC ACID

BY E. A. BUDGE

RECEIVED NOVEMBER 23, 1931 PUBLISHED MAY 7, 1932

The decomposition of hydrogen peroxide into oxygen and water in the presence of hydrochloric acid has been studied recently by Livingston and Bray,[1] who measured the concentration of peroxide after various time intervals by titration with permanganate, and also by Maass and Hiebert,[2] who followed the reaction by measuring the rate of evolution of oxygen. Both pairs of investigators worked mainly at 25° and found the reaction to be unimolecular with respect to the hydrogen peroxide. Maass and Hiebert, however, obtained velocity coefficients which differed from those of Livingston and Bray for (presumably) identical conditions and they also found a well-marked period of acceleration for the more concentrated solutions. In Fig. 1 some of the values obtained by these workers are shown in the one graph, values of log k being plotted as ordinates and the concentration of hydrochloric acid (in g. moles per liter) as abscissas. Curve I shows some of Livingston and Bray's results and Curve II some

[1] R. S. Livingston and W. C. Bray, THIS JOURNAL, **47**, 2069 (1925).

[2] O. Maass and P. G. Hiebert, *ibid.*, **46**, 290 (1924).

of those of Maass and Hiebert, both at 25°. The other curves will be referred to later.

The present author was prompted to study the same reaction since the inconsistency in these results seemed to be in accord with certain mathematical investigations carried out by him,[3] in which it is shown that in the case of consecutive reactions it is possible for experimental reaction velocity coefficients to have different values according as they are based on measurements of reactants or of resultants. The coefficient by resultant may show an initial acceleration, whereas that by reactant shows no disturbance whatever. Certain types of catalysis, supersaturation of solution with respect to gaseous resultant, and initial changes of temperature due to heat effects on mixing may also cause similar initial disturbances.

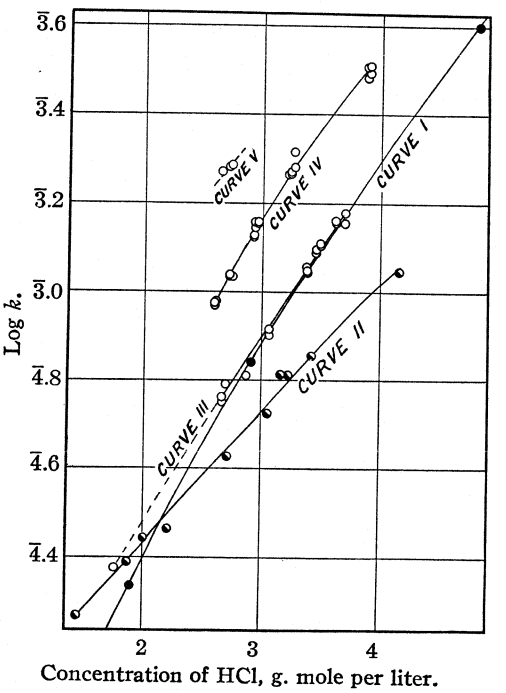


Fig. 1.—Variation of k with temperature and concentration of hydrochloric acid.

Accordingly, experiments were carried out using methods practically the same as those used by Livingston and Bray and by Maass and Hiebert. The two methods were made as comparable as possible by preparing the reaction mixture, bringing it rapidly to the temperature of the bath and dividing it between the two reaction vessels, which were placed side by side in the same bath. In preparing these mixtures commercial 3% hydrogen peroxide and C. P. hydrochloric acid were used. The hydrochloric acid was freed from a trace of impurity (probably iron chloride) by letting it stand for some hours with hydrogen peroxide and then twice distilling, the constant-boiling fraction alone being used. Since the methods were directly compared and the values obtained agreed well with those of Livingston and Bray, further purification of materials was considered unnecessary.

The gas evolution apparatus used by Maass and Hiebert was modified by omitting the tubes of concentrated sulfuric acid and potassium iodide solution and a simpler method of calculating the velocity coefficients was employed. "Instantaneous" values of the unimolecular velocity coefficient were obtained by dividing the rate of evolution of oxygen (in cc. per minute) by the total volume of oxygen (in cc.) yet to be evolved from the instant of the measurement until complete decomposition of the peroxide. This

[3] E. A. Budge, "Reports of the Australasian Association for the Advancement of Science," Hobart Meeting, January, 1928, XIX, 147.

necessitated continuing the reaction to near completion and then estimating the residual peroxide. This was done either by heating the reaction mixture to near boiling until the peroxide was decomposed or by titration of an aliquot part of the reaction mixture by permanganate. To render the measurements involved in this method less tedious, an automatic bubble counter[4] was developed and used. From the readings of this instrument the rate of evolution of oxygen (in bubbles per minute) and also the total volume of oxygen (in bubbles) up to the instant of measurement were easily obtainable.

Throughout the investigation the concentration of hydrochloric acid in the reaction mixtures was measured by the Iceland spar method.[5] In some cases this was checked by precipitation of silver chloride with concordant results.

The results obtained by the titration method showed a very constant unimolecular coefficient which agreed well with those given by Livingston and Bray for corresponding conditions. The results obtained by the gas evolution method showed a well-marked period of acceleration (lasting from forty to eighty minutes) and thereafter a constant unimolecular coefficient, which was practically identical with that given by the titration method. This period of acceleration has since been shown to be due (at least in part) to supersaturation of the reaction mixture with oxygen.[6]

Accordingly, a new apparatus for the gas evolution method was installed with the object of testing whether there were any irregularity other than that due to supersaturation. A diagram of this apparatus is shown in Fig. 2.

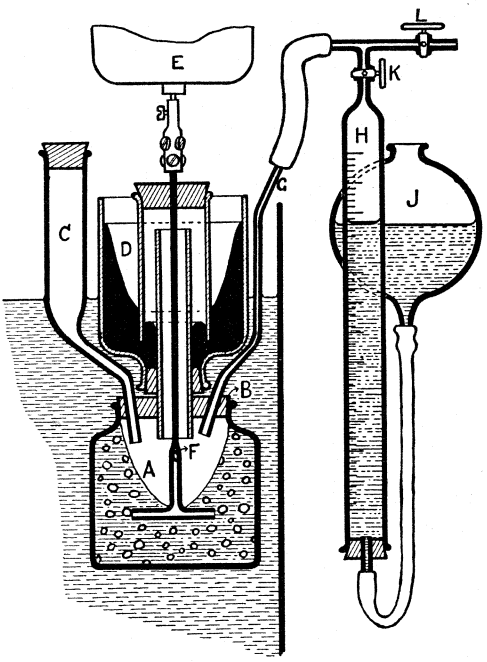


Fig. 2.—Apparatus for measurement of speed of gas evolution (not to scale).

In this apparatus a wide-mouthed bottle A was used as reaction vessel. The mouth of this was closed by a trebly-bored rubber stopper B, which was firmly clamped in position (the clamps are not shown in the diagram) and had its lower surface covered with vaseline. The reagents were added to the bottle through tube C, which was closed by a well-fitting rubber stopper. The middle hole of the rubber stopper carried a mercury seal D and allowed the entrance of the stirrer, which was directly coupled to the shaft of a small motor E. For most of its length the stirrer was of solid glass rod, but, about 5 cm. from the bottom, a T-shaped piece of glass tubing was sealed on and this was provided with a small hole at F. This stirrer, which was rotated at about 1000 r. p. m., proved very efficient in overcoming supersaturation. On account of centrifugal action, gas from the top of the bottle entered

[4] E. A. Budge, THIS JOURNAL, **53**, 2451 (1931).

[5] D. O. Masson, *Chem. News*, **81**, 73 (1900).

[6] The author is much indebted to Professor Bray and Mr. B. Makower for suggesting this possibility.

at the hole F and was discharged in a constant stream of bubbles through the open arms of the T-piece. Thus not only was the liquid violently agitated but also it was continually charged with a multitude of small gas bubbles. The third hole in the rubber stopper B carried a tube G leading to the gas buret H, which was filled with water and connected to the counterpoised leveling bulb J. The stopcocks K and L facilitated the manipulation of this part of the apparatus.

The apparatus was used as follows. The charge of peroxide was placed in the vessel A after the stirrer had been adjusted to run steadily without vibration and the apparatus had been placed in position in the bath and proved free from leakage. When this peroxide had reached the temperature of the bath and while the stirrer was running at full speed, the necessary hydrochloric acid was added as rapidly as possible by means of the tube C, which was at once stoppered. On account of the heat of dilution of the acid, it was necessary to determine by previous trial what its temperature must be before addition in order that the temperature of the mixture in the bottle should be the same as that of the bath immediately after the addition. The zero time for the reaction was taken as the instant when half of the acid had been added and measurements of the rate of evolution of oxygen were begun as soon as possible. To make one of these measurements, the stopcocks K and L were opened and J raised until the level of the water was near the top of the buret. After noting the reading of the buret, the stopcock L was closed at a noted instant. As the oxygen accumulated in H, J was lowered to keep the pressure of the gas roughly that of the air outside. When a suitable volume of gas had been collected, K was closed at a noted instant and when the two water menisci were on the same level and the volume of gas was read off. If the readings are taken quickly, several measurements of the rate of gas evolution can be made in quick succession without expelling the gas from the buret. While both K and L are closed, the pressure in the rest of the apparatus rises slightly, but, on opening K again and lowering J, this excess pressure is relieved and a second reading can be taken. The volume of gas collected was corrected for pressure and temperature and divided by the time during which the gas had been collected. This furnished the rate of evolution of oxygen in cc. per minute; this rate of evolution was considered to measure the speed of the reaction at the instant midway between the instants of closing stopcocks L and K. Where several repetitions (usually overlapping one another) were made as described above, the average of the rates was used for further computation. By opening K and L and raising J, the gas collected in the buret was expelled and the apparatus made ready for further rate measurements.

From the values of the speed of reaction at various times thus obtained the unimolecular reaction velocity coefficient was obtained by plotting the logarithm of the speed (in cc. per minute) against the time (in minutes) from the zero of the reaction. The points plotted should lie on a straight line if the reaction is truly unimolecular. The velocity coefficient is obtained by multiplying the slope of the line by -2.303. This method is especially convenient for studying the early stages of the reaction as it does not necessitate continuing the experiment after sufficient readings have been made to determine the straight line with sufficient accuracy. Also, the method is not affected by what happens to the reaction mixture between readings, provided that its temperature remains constant and that the stirrer has been running for a sufficiently long time before making the reading to overcome supersaturation. This method was subsequently used to recalculate the results of the

previous gas evolution experiments; the results agreed well with those of the former method.

The period of acceleration was now very much shorter (from three to fifteen minutes) and, since it was very variable in duplicate experiments and was reduced by higher speed of stirring, it is considered to be almost entirely, if not entirely, due to supersaturation. In any case, it is too short to enable sufficiently accurate rate measurements to be made to permit its use in determining the mechanism of the reaction. Table I gives the condensed results of one experiment by this method. The number of the reading is given in column 1, the time in minutes from the zero of the reaction

TABLE I

Run G47. June 8, 1931. Temperature of bath, 25.00°. Reaction mixture: 181 cc. of hydrogen peroxide (3%) at 25.0° to which was added 196 cc. of HCl (dilute) at 15.8°, giving a mixture containing 3.282 g. mole of HCl per 1000 g. and 0.44 g. mole of H_2O_2 per liter at 25.0°.

Reading number	Time, minutes	Time of collection, minutes	Oxygen, cc.	Speed of reaction in cc. of O_2 per minute
1	1.5	0.83	1.01	1.22
2	2.3	2.45	3.04	1.24
3	2.7	3.32	5.16	1.55
4	3.4	4.55	8.78	1.93
5	3.7	5.25	10.73	2.05
6	4.1	6.08	13.21	2.18
7	4.6	6.92	15.57	2.25
8	5.1	8.00	18.08	2.26
9	5.4	8.58	20.26	2.36
10	5.7	9.25	22.00	2.38
11	6.2	10.22	24.70	2.41
12	6.8	11.43	28.02	2.45
13	7.2	12.18	30.08	2.47
14	7.6	12.97	32.20	2.48
15	8.0	13.80	34.52	2.50
		4.50	12.49	
16	20.0	5.70	15.93	2.78
		6.75	18.79	
		1.58	4.36	
17	31.2	3.03	8.12	2.71
		4.12	11.12	
		4.08	10.96	
18	38.3	5.17	13.97	2.70
		6.17	16.55	
		7.00	19.07	
		4.08	10.55	
19	51.6	5.13	13.37	2.60
		7.42	19.28	
		4.67	11.28	
20	104.1	6.17	14.91	2.41
		8.83	21.07	

TABLE I (*Concluded*)

Reading number	Time, minutes	Time of collection, minutes	Oxygen, cc.	Speed of reaction in cc. of O_2 per minute
21	148.5	4.95	11.02	2.22
		5.97	13.28	
		7.57	16.74	
22	169.7	5.33	11.43	2.15
		6.47	13.98	
		7.60	16.33	
23	202.7	7.47	15.43	2.07
		8.83	18.27	
		10.00	20.79	
24	221.4	6.30	12.58	2.00
		8.50	16.86	
		9.75	19.56	
25	259.3	5.60	10.48	1.88
		7.25	13.71	
		10.33	19.30	

to the middle of the collection period in column 2, the duration in minutes of the collection period in column 3, the volume of the collected oxygen (in cc., corrected for pressure and temperature) in column 4 and the rate of evolution of oxygen (in cc. per minute) in the last column. The horizontal lines show when the gas was discharged from the buret. At the beginning of this experiment the stirrer was run at low speed; just before reading number 17 it was speeded up; before 19 it was slowed again; before 22 speeded up; before 24 slowed down again and between 24 and 25 it was stopped altogether for seventeen minutes and then run at full speed. This was to test the efficiency of the stirrer in overcoming supersaturation. The plot of these measurements is shown in Fig. 3, the logarithm of the rate of evolution of gas being plotted as ordinate and the time from zero as abscissa.

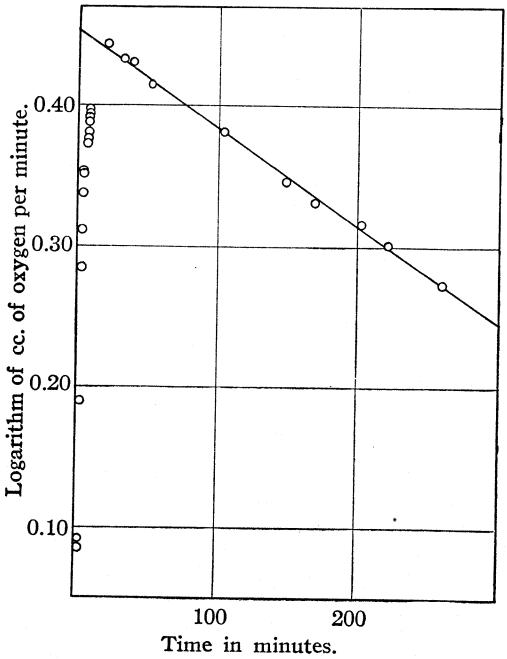


Fig. 3.—Graphical evaluation of k from measured speed of gas evolution.

The constancy of the velocity coefficient by reactant in the early stages of the reaction was also investigated by a titration method. A measured weight of hydrogen peroxide solution of known titer was placed in a weighing bottle and hung in the bath. At zero time a suitable volume of hydrochloric acid of known concentration was added to the weighing bottle and the weight of acid added was determined by weighing its containing vessel (a stoppered U-tube) before and after the addition of acid. The temperature of the acid was so adjusted before addition that the heat of dilution of the acid just brought the temperature of the mixture to that of the bath. Meanwhile a large beakerful of dilute sulfuric acid had been tinted to a suitable end-point by permanganate. Half of this was reserved for comparison to define the end-point of the titration and to the other half there was added from a weighed weight buret standard permanganate in quantity slightly less than that needed to react with the peroxide in the weighing bottle. At the expiration of the desired reaction period, the weighing bottle was removed from the bath and rapidly washed on the outside with distilled water. The stopper was then removed, the bottle and contents were added to the beaker containing the permanganate solution and the titration then finished so that the tint of the solution matched the blank. From the weight of permanganate solution required and the known titer of the peroxide before addition of acid, the fraction of the peroxide remaining undecomposed could be calculated. Also the concentration of hydrochloric acid in the mixture was calculated. By this means a number of results were obtained for the one reaction period and slightly differing concentrations of acid. The fraction of the peroxide undecomposed at the end of the reaction period was then interpolated graphically for some chosen acid concentration. By a repetition of this process for other reaction periods, ranging from two to forty-five minutes, values were obtained for the fraction of the peroxide undecomposed for a series of times and all for the one acid concentration. The method was very tedious but as far as could be seen the results were exact. On plotting the logarithm of the fraction of peroxide undecomposed against the reaction time, a straight line was obtained in each series of experiments. Hence no measurable irregularity was found in the velocity coefficient as determined by titration of the peroxide, even in the early stages of the reaction.

Table II contains in condensed form the results of all the present experiments in which there are no known sources of gross inaccuracy. In this table the distinguishing number of the experiment is given in column 1. Experiments in which the peroxide was determined by titration are distinguished by T, those in which the rate of evolution of oxygen was measured by G, those in which the rate of evolution of oxygen was measured by bubble counter by B, and two series in which weight titration by permanganate was used are distinguished by W. The concentration of hydrochloric acid in gram molecules per 1000 g. of reaction mixture is given in column 2. The approximate initial concentration of hydrogen peroxide in gram molecules per liter is given in column 3. The total duration of the experiment is given in column 4 and the value of the unimolecular velocity coefficient (k) is given in column 5.

In Fig. 1 these results are shown graphed along with those results of Livingston and Bray[1] and of Maass and Hiebert[2] which fall within the limits of the graph. In this figure, values of log k are plotted as ordinates and concentration of hydrochloric acid as abscissas. Curve I shows Livingston and Bray's results at 25°; Curve II shows Maass and Hiebert's

TABLE II

COLLECTED RESULTS OF EXPERIMENTS ON THE SPEED OF DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF HYDROCHLORIC ACID

Expt.	Concn. of HCl	Concn. of peroxide	Duration of expt.	$k \times 10^4$
		Experiments at 25°		
G53	1.714	2.62	210 min.	3
T20	2.566	0.93	25 hours	7.2
G20	2.566	.93	26 hours	7.1
G36	2.598	.64	220 min.	7.8
W2	2.75		7 min.	8.1
T21	2.908	.81	24 hours	10.43
B21	2.908	.81	22 hours	10.4
G41	2.911	.56	150 min.	10
T18	3.212	.83	22 hours	14.4
B18	3.212	.83	22 hours	14.1
T19	3.213	.86	27 hours	14.4
B19	3.213	.86	27 hours	14.0
G49	3.28	.43	135 min.	15.6
G47	3.282	.44	260 min.	15.5
T17	3.282	.89	17 hours	15.7
B17	3.282	.89	18 hours	15.5
T16	3.308	.91	20 hours	16.1
B16	3.308	.91	20 hours	16.0
T15	3.425	.91	18 hours	18.2
B15	3.425	.91	16 hours	18.0
W1	3.50		45 min.	18
		Experiments at 30°		
			Hours	
T10	2.494	0.90	25	11.9
G10	2.494	.90	25	11.7
T11	2.500	.89	27	12.0
G11	2.500	.89	27	11.8
T9	2.607	.59	25	13.8
G9	2.607	.59	26	13.7
T8	2.626	.56	25	13.6
G8	2.626	.56	25	13.7
T5	2.801	.92	25	16.9
G5	2.801	.92	22	16.8
T3	2.810	.93	15	17.55
G3	2.810	.93	19	18
T4	2.828	.94	18	17.95
G4	2.828	.94	18	18
T6	3.045	1.20	22	23.0
T2	3.082	1.28	25	23.5
G2	3.082	1.28	25	23.2
T1	3.102	1.28	26	26
G1	3.102	1.28	21	24
T13	3.651	0.66	9	40.4
G13	3.651	.66	19	38
T12	3.667	.68	19	40.5
G12	3.667	.68	19	39

TABLE II (*Concluded*)

Expt.	Concn. of HCl	Concn. of peroxide	Duration of expt.	$k \times 10^4$
		Experiments at 35°		
G46	2.549	0.31	260 min.	23.5
G44	2.602	.27	330 min.	24.0
G45	2.617	.31	315 min.	24.2

results at 25°; the results of the present investigation are shown in Curves III (25°), IV (30°) and V (35°). It will be seen that the present results are in good agreement with those of Livingston and Bray and quite discordant with those of Maass and Hiebert.

The Temperature Coefficient

Livingston and Bray[1] state that the temperature coefficient of the reaction is 3.60 for a rise of temperature of 10°. This value is based on their measurements at 25 and 40°. The method of calculation used by them appears, however, to be incorrect, in that they have assumed the ratio of velocity coefficients for two temperatures 10° apart to be two-thirds of the ratio of coefficients for temperatures 15° apart. A preferable procedure would seem to be based on the well-known Arrhenius formula

$$\log (k_2/k_1) = A(1/T_1 - 1/T_2)$$

Calculation of the constant A in this expression from Livingston and Bray's data leads to $A = 4500$ and the ratio $k_{35°} : k_{25°}$ derived from this is about 3.1. The results of the present investigation also permit of the calculation of a temperature coefficient. That derived from measurements at 25° and 30° is 3.1, A being 4550. The measurements at 35° are fewer and less reliable than the others but the value of the temperature coefficient derived directly from the measurements at 25 and 35° is 3.25, which leads to $A = 4700$. The value (3.60) given by Livingston and Bray is therefore certainly too high and the true value is in the neighborhood of 3.1.

The author desires to express his sincere thanks to Professor E. J. Hartung for the generous manner in which he has made available facilities for carrying on this work and for his very helpful criticism and advice.

Summary

The decomposition of hydrogen peroxide in the presence of hydrochloric acid has been studied over a moderate range of concentrations at temperatures of 25, 30 and 35°, by methods which have involved measurements of both the residual peroxide and of the rate of evolution of oxygen.

1. The velocity coefficients obtained agree closely with those of Livingston and Bray and disagree with those of Maass and Hiebert.

2. When the concentration of the residual peroxide is measured, the reaction is strictly unimolecular from the first within the limits of measurement.

3. When the rate of evolution of oxygen is measured, the reaction is strictly unimolecular after a very short period of acceleration which is ascribed to supersaturation.

4. The temperature coefficient of the reaction is about 3.1.

5. A method of weight titration of hydrogen peroxide by permanganate is described which enabled reaction velocity measurements to be carried out in the very early stages of the reaction.

6. A graphical method is described which enables unimolecular velocity coefficients to be calculated from measurements of the rate of evolution of gas without any knowledge of the total volume of gas evolved or the exact concentration of the peroxide.

It is believed that both these methods are new.

MELBOURNE, VICTORIA, AUSTRALIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 279]

ABSORPTION SPECTRA AT HIGH PRESSURES AND AT LOW TEMPERATURES. THE TRANSPARENCY OF ARGON AND METHANE[1]

BY B. J. EISEMAN, JR.

RECEIVED NOVEMBER 24, 1931 PUBLISHED MAY 7, 1932

The purpose of this investigation was to study the absorption spectra of a number of substances whose pressure, volume, and temperature relations suggested the possibility of molecular aggregation as a factor in the attempt to account for the physical properties at high concentration and at low temperature. Since it was not possible to predict the spectral region of the absorption of the supposed associated or aggregated molecular species, the spectral region selected was the visible and the quartz ultraviolet, where absorption may be most readily studied. In this paper we shall describe the design of apparatus found satisfactory for the purpose and the results of the studies with argon and methane.

Method.—The light absorption was determined by the method of photographic spectrophotometry. The relative blackening of the photographic plate served as a measure of the light transmission through the empty absorption tube and through the tube filled with fluid.

An Adam Hilger E 1 spectrograph with glass and quartz optical system was used for photographing the spectra. Exposures were twenty minutes to one hour for slit widths of 0.01 to 0.02 millimeter.

An under-water spark served as a source of continuous light. However, the usual aluminum and copper electrodes were replaced advantageously by magnesium electrodes for the shorter wave lengths. In later work we have used the hydrogen discharge tube as

[1] The results presented here are to be found in greater detail in the Ph.D. Thesis of B. J. Eiseman, Jr., Massachusetts Institute of Technology, 1927.

a source of continuous ultraviolet radiation. For the visible region, a tungsten ribbon heated with 18 amperes at 6 volts in a nitrogen filled glass bulb was very satisfactory.

The iron spark and iron arc spectra were used for obtaining reference lines for determining the wave lengths.

It is doubtful whether a continuous absorption amounting to less than 10% would have been detected with the procedure described.

Absorption Tubes.—A fused quartz Dewar tube of special design was used to contain the refrigerant and absorption tube during loading and for the low temperature absorption measurements. Two tubulations, opposite each other, in the double walls of the Dewar tube permitted the insertion of an absorption tube through the body of the Dewar tube. Figure 1 shows the Dewar tube with the quartz absorption tube (I), used for the low-temperature measurements. Two quartz tubes (T and T′), each with a plane window (W and W′) fused on at one end, and the other end open, were fused into another quartz tube (L) of slightly larger diameter to complete the absorption tube, in which all three tubes (T, T′ and L) are coaxial. A side tube (C) on the larger tube connected to the vacuum line and loading system by means of a quartz–Pyrex graded seal. The windows (W and W′) were 15 millimeters apart and the bore of the larger tube (L) was 10 millimeters. The refrigerant was prevented from escaping through the small clearance space between the tubulations and the absorption tube by packing moistened asbestos fiber (A) in this space. After the asbestos had dried, rubber tape (R) was wound around the ends of the tubulations and the projecting arms of the absorption tube. A stream of dry nitrogen was passed through N at each end of the absorption tube. In an earlier design tubes T and T′ were replaced by quartz rods. However, the ultraviolet transmission was not so satisfactory as in the arrangement described above.

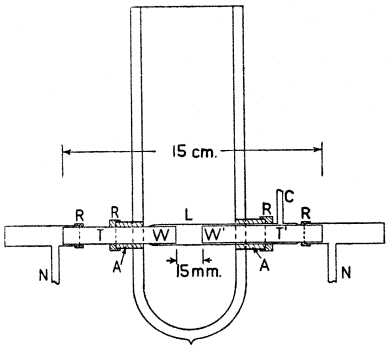


Fig. 1.

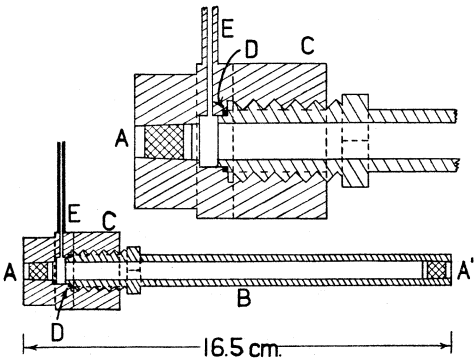


Fig. 2.

Steel absorption tubes with fused-quartz windows were used for the examination of gases at high pressures. In Fig. 2 the tube II was of high tensile strength machine steel. It consisted of two parts (B and C) which could be screwed together. The longer section (B) had an outer diameter of 11 millimeters and a bore of 7.3 millimeters. The bore was tapered at one end to take one of the windows (A′). The other window (A) was in a hexagonal cap (C). An aluminum washer, D, the cross section of which was 1 millimeter square, rendered the tube tight when compressed between B and C. The assembled tube had a light path of 14.4 centimeters. Connection to the vacuum and loading system was made through E, which was silver soldered to C. The truncated cones (A and A′) were of transparent fused quartz, the end faces being polished plane, parallel to each other and perpendicular to the axis of symmetry of the

steel tube. A and A′ were carefully ground into their respective tapers in the steel tube by carrying out the preliminary grinding in several replicas of the tapers of the steel tube. The final light grinding was done in the steel tube tapers. The larger faces of the quartz cones were about 8 millimeters in diameter, the taper was about 3° and the height of the truncated cone about 1 centimeter. A number of unsuccessful attempts to produce a tube of this design capable of withstanding a pressure of 500 atmospheres resulted from non-uniform contact between the steel and quartz. In these cases the windows were shattered or so pulverized internally as to become practically opaque upon application of pressure. Inasmuch as the windows are displaced about 0.5 mm. as the pressure is raised to 500 atmospheres, it is very essential that the peripheries of the faces be round chamfered to prevent chipping. The windows were pressed firmly into the steel tapers covered with molten "picein," and tested with an oil injector. During the testing most of the "picein" was extruded, leaving a bright metallic contact surface. The tubes were vacuum tight and could be evacuated so that the pressure rose to only 0.001 millimeter of mercury on standing overnight. The steel absorption tube was of sufficiently small outside diameter to fit into the tubulation of the quartz Dewar tube mentioned above.

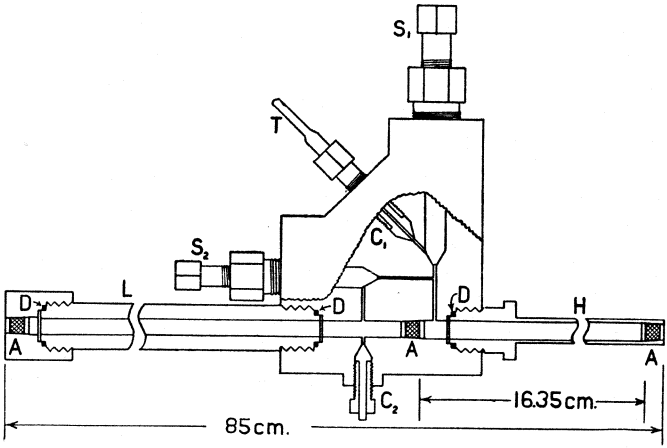


Fig. 3.

A special tube (III) was built for studying Beer's law at high pressures. The general construction was as described for steel tube II. Figure 3 shows a steel absorption tube with three quartz windows (A) affording two absorption chambers of the same internal diameter in tandem. Connection to the vacuum and loading system was made through T, with steel stopcock S_1. The fluid contained in the shorter tube (H) could be expanded to fill both chambers (H and L) by opening stopcock S_2. This afforded a considerable change in density of the fluid accompanied by only a slight change in the amount of matter in the light path. The sum of the internal lengths of the absorption chambers was 81.97 centimeters and the internal length of the short absorption chamber was 16.35 centimeters. The ratio of these lengths was 5.013 and the ratio of the corresponding volumes about 3% less. This tube will be referred to as the double steel tube.

Argon

Shaver[2] found that a column of gas at 140 atmospheres' pressure and 35 centimeters long containing 80% argon and 20% nitrogen was transparent

[2] W. W. Shaver, *Trans. Roy. Soc. Canada*, **16**, III, 135 (1922).

from 7000 to 2150 Å. E. Meyer[3] believed that his measurements showed a slight absorption in the ultraviolet due to gaseous argon at low pressure. Dolezalek,[4] from a study of the vapor pressures of mixtures of argon and nitrogen, concluded that liquid argon contained a considerable proportion of A_2.

Liquid argon was examined, since any absorption that might be found would be that of an aggregate and thus of considerable interest.

Procedure.—The argon, supplied in a glass bulb, by the Research Laboratory of the General Electric Company, was specified to be of a high purity. It was manipulated in a glass vacuum line by the use of liquid air at reduced pressure and distilled into the quartz absorption tube (I) in the tubulated Dewar flask containing liquid air.

Results and Discussion.—Liquid argon at about $-180°$ and 135 centimeters of mercury pressure was examined from 6780 to 2450 Å. Argon, as a glassy solid at about $-190°$ and 20 centimeters of mercury pressure, was examined from 2490 to 2130 Å. No absorption was found. Accordingly, argon exercises no sensible selective absorption in the region examined, and if there is a general absorption it must be very small. If aggregates form in appreciable quantity, their absorption does not lie within this spectral region.

Methane

Glockler[5] found a length of 54 centimeters at atmospheric pressure of methane to be transparent to 2400 Å. Dennison and Ingram[6] found a length of 10 meters of methane at 70 centimeters pressure of mercury to have one absorption band (8800 to 9000 Å.) in the region from 6500 to 9500 Å.

For this investigation the methane was prepared by the method of Keyes, Smith and Joubert[7] and loaded into the short steel tube (II). The methane was examined at a pressure of 400 atmospheres at 20° from 6900 to 2150 Å. It was also examined at this concentration, but at a temperature just above that of the disappearance of the liquid phase, from 4500 to 3240 Å. No absorption was found and the conclusions are identical with those for argon.

Acknowledgment.—I wish to thank Professor F. G. Keyes under whose guidance this work was carried out, Dr. R. H. Gerke who suggested the problem, and Professor Louis Harris for his assistance.

Summary

Apparatus for the examination of the absorption spectra of liquefied

[3] E. Meyer, *Verhandl. deut. physik. Ges.*, **2**, 362 (1904).
[4] F. Dolezalek, *Z. physik. Chem.*, **93**, 585 (1918–1919).
[5] G. Glockler, *Proc. Nat. Acad. Sci.*, **11**, 74 (1925).
[6] D. D. Dennison and S. B. Ingram, *Phys. Rev.*, **36**, 1451 (1930).
[7] Keyes, Smith and Joubert, *J. Math. Phys., Mass. Inst. Tech.*, **1**, 192 (1922).

gases at low temperatures and of fluids up to 500 atmospheres in the visible and quartz ultraviolet has been described.

Argon and methane have been found to be transparent at high concentration in that spectral range.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 280]

THE TRANSMISSION OF LIQUID CARBON DIOXIDE

BY B. J. EISEMAN, JR., AND LOUIS HARRIS

RECEIVED NOVEMBER 24, 1931 PUBLISHED MAY 7, 1932

Preliminary measurements by one of us[1] seemed to indicate a continuous absorption of ultraviolet light by liquid carbon dioxide at room temperature. These measurements were made with the short steel absorption tube.[2] The double steel tube,[2] in which the product of length times density was the same through the liquid and gaseous carbon dioxide, gave the same results. When liquid carbon dioxide filled the short arm (16.35 cm.), there was absorption below 3000 Å.; when this liquid was expanded to a gas so that the original mass was distributed over a length of 81.97 cm., no absorption was observed. Upon recondensing this carbon dioxide to a liquid in the short arm, the absorption reappeared. The conclusion seemed inevitable that some molecular species, probably $(CO_2)_x$, was present in large quantity in the liquid carbon dioxide and absorbed in the ultraviolet. However, after the short arm of the double steel tube had been flushed with liquid carbon dioxide a number of times and the carbon dioxide given more careful purification, the results could not be duplicated. The absorption in the liquid carbon dioxide seemed to be a strange function of the density and eventually disappeared abruptly except perhaps for a slight continuous absorption below 2500 Å. Liquid carbon dioxide containing water (introduced intentionally) showed a slight absorption (beginning around 2650 Å.) which disappeared on vaporizing. (The accuracy of these early measurements was not better than about 10%.) It was necessary to conclude that the absorption in the liquid was due to some dissolved impurity. Whether the impurity causing the absorption was picked up in the absorption tube or was present in the gas originally introduced has not been settled by this work.

Shortly after this phase of the work had been completed, an article by Harig[3] appeared on the ultraviolet absorption of liquid carbon dioxide. His results were similar to our early experience except that he found

[1] B. J. Eiseman, Jr., Ph.D. Thesis, M. I. T., 1927.

[2] B. J. Eiseman, Jr., THIS JOURNAL, 54, 1778 (1932).

[3] Harig, *Physik. Z.*, 30, 8 (1929).

even more absorption in liquid carbon dioxide. A two-millimeter length of liquid carbon dioxide was sufficient to absorb nearly all radiation below 2600 Å. He found no absorption in a 110-cm. layer of gaseous carbon dioxide at 60 atmospheres. No matter what the conditions of temperature or pressure might be, he found absorption as long as liquid carbon dioxide was present and none through the gaseous carbon dioxide. He concluded that a polymer $(CO_2)_x$ was present in the liquid carbon dioxide. In the light of our later experience it seemed very certain that Harig was measuring the absorption of some impurity soluble in liquid carbon dioxide. We decided to repeat our measurements in such a way as to avoid all contact of carbon dioxide with grease, oil or any other substances likely to be dissolved by carbon dioxide and thus try to check our later measurements independently.

Preparation of Carbon Dioxide.—Carbon dioxide was prepared by heating sodium bicarbonate. Most of the water was removed by cooling and the last traces of water removed with phosphorus pentoxide. The carbon dioxide was sublimed very slowly three times, first and last portions being discarded each time. The carbon dioxide was stored in large glass bulbs connected to a quartz spiral manometer. Carbon dioxide was introduced from the bulbs into the absorption tube by breaking a tip in a glass valve. (All valves were of this type.) The carbon dioxide was never in contact with grease, cements, or metal.

Apparatus and Manipulation.—The "low temperature" absorption tube[2] was used for these measurements. Instead of blowing nitrogen on the windows to prevent frost, it was found much more advantageous to add two extra quartz windows to the absorption tube after it had been assembled in the tubulated Dewar tube. The spaces between these extra windows and the windows of the absorption tube were evacuated. There was never any tendency for frost to form on the windows although the body of the absorption tube was kept at $-50°$ for hours. In order to determine the transmission of the absorption tube empty, the lead from the absorption tube was connected to a trap in which the carbon dioxide could be frozen. The absorption tube with this trap attached was sealed off from the pumping system and carbon dioxide reservoir after sufficient (calculated from the known volumes and the change in pressure) carbon dioxide had been loaded into the trap. This arrangement permitted many observations of the transmission, with the tube full or empty, to be made with one sample of carbon dioxide without changing the position of the absorption tube. Solid carbon dioxide–alcohol was the refrigerant used in the tubulated Dewar surrounding the absorption tube, while liquid air was used for freezing out the carbon dioxide in the adjoining trap. At the carbon dioxide triple point ($-56.6°$) the pressure is 5.2 atmospheres and since it was necessary to make measurements at more elevated temperatures, it was gratifying to find that the absorption tube would withstand pressures up to 10 atmospheres.

The absorption of liquid carbon dioxide was determined at $-51°$. Although the length of this absorption tube (1.5 cm.) was about one-tenth the length we used previously (ten times the length of the tube used by Harig) the increased density and the lower temperature would certainly favor the formation of carbon dioxide aggregates.

Spectrograms were made with the tube empty and the tube full using a Hilger E 315 spectrograph. A hydrogen discharge tube served as a source

of light. The plates were photometered with the aid of microphotometer lent by Professor G. R. Harrison. The accuracy of the final measurements was within a few per cent. No absorption was observed from 6000 to 2150 Å.

Note.—The last filling of the double steel tube with carbon dioxide was in December, 1928. It was left in January, 1929, with liquid carbon dioxide in the shorter arm. In January, 1931, the amount of liquid was still the same as when it was left two years earlier.

Conclusions

Liquid carbon dioxide (1.5 cm. layer) at $-51°$ has been found to be transparent to the visible and quartz ultraviolet. A 16.35-cm. layer of liquid carbon dioxide at room temperature was also found to be transparent except perhaps for a slight continuous absorption below 2500 Å.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES AT PITTSBURGH]

THE KINETICS OF GAS EXPLOSIONS. II. THE THERMAL REACTION BETWEEN OZONE AND HYDROGEN BROMIDE[1]

BY BERNARD LEWIS[2] AND W. FEITKNECHT[3]

RECEIVED NOVEMBER 30, 1931 PUBLISHED MAY 7, 1932

It was suggested[4] that the oxygen atom and an active oxygen molecule are the carriers in the reaction chains involved in the thermal decomposition and explosion of ozone sensitized by bromine vapor.[4,5] In an attempt to detect the presence of free oxygen atoms during this reaction, hydrogen bromide[6] was added to the mixture, since it is known to react easily with the former.[7] It was found, however, that ozone reacts with pure hydrogen bromide so rapidly that the chains in the ozone–bromine reaction are dwarfed in comparison with the fast and long chains in this new ozone–hydrogen bromide reaction.

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before the American Chemical Society, Buffalo, Sept., 1931.

[2] Physical Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Consultant Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[4] Part I. Lewis and Feitknecht, THIS JOURNAL, **53**, 2910 (1931).

[5] Lewis and Feitknecht, *Z. physik. Chem.* Bodenstein-Festband, 113 (1931). See also Lewis and Schumacher, *ibid.*, **138A**, 462 (1928); **6B**, 423 (1930); *Z. anorg. Chem.*, **182**, 182 (1929); *Z. Electrochem.*, **35**, 651 (1929).

[6] Lewis and Feitknecht, THIS JOURNAL, **53**, 3565 (1931). The effect of hydrogen will be described elsewhere.

[7] Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931).

Preliminary experiments indicated that when ozone is added to hydrogen bromide at a pressure of 10 mm. for each gas, an explosion occurs immediately, the hydrogen bromide is oxidized to water vapor and bromine, and any excess ozone is also destroyed. The same action occurs even at temperatures of -77 and $-104°$ at slightly increased pressure. Below the limiting pressure the two gases react at these low temperatures at a fast but measurable rate.

A detailed and comprehensive kinetic study of this reaction disclosed its initial heterogeneity, despite its enormous velocity. The facts leading to the conclusion that the reaction chains start at the walls and then propagate into the gas phase are similar to those given in Part I[4] of this investigation. In this paper we shall therefore omit detailed experiments but shall point out certain differences and similarities with the ozone–bromine reaction.

Apparatus and Materials.—The apparatus used was the same as described earlier.[4,8] A Pyrex glass cylindrical reaction vessel 3.5 cm. in diameter and 12 cm. long was used for most experiments. The low-temperature baths used were carbon dioxide–ether ($-77°$) and boiling ethylene ($-104°$). Pure hydrogen bromide was prepared from resorcinol and bromine[9] and was purified by low-temperature distillation. It was kept in the solid state when not in use. Greaseless, non-corrosive needle valves were used in the apparatus to by-pass gases. Pure ozone was prepared as before.[4,5]

Experimental Procedure.—The reaction could be followed by measuring the decrease in pressure, since the products, water and bromine, have negligible vapor pressures at the low temperatures used. Separate experiments indicated that any reaction between water and hydrogen bromide to form a solid hydrate was negligible.

Usually hydrogen bromide was admitted to the reaction vessel first. At first the pressure increased, and if the initial pressure was above the explosion limit an explosion occurred after a lag of about two seconds. Just below the explosion limit the reaction was complete in ten to twenty seconds after the initial rise in pressure. At considerably lower pressures lag periods varying from three to forty seconds were observed.

For the same pressure and composition the rate of reaction was faster when ozone was admitted first. This probably means that the initial surface adsorption layer, with ozone already adsorbed, favors the initiation of a larger number of chains.

The Non-explosive Reaction.—With an excess of ozone the decrease in pressure in the non-explosive reaction corresponds to the amount of hydrogen bromide used, whereas with excess hydrogen bromide it is approxi-

[8] Lewis and Schumacher, *Z. Elektrochem.*, **35**, 651 (1929).

[9] Ephraim and Schärer, *Ber.*, **61**, 2164 (1928).

mately twice as great as the ozone used. This and other data suggest that the reaction follows approximately[10] the formula.

$$2HBr + O_3 = H_2O + Br_2 + O_2 \qquad (1)$$

The non-explosive reaction and the lag period preceding it are largely influenced by the activity of the wall. A large increase in activity is obtained when the reaction products of a preceding reaction are left frozen out on the wall.[11] The activity increases as the thickness of the layer increases. It reaches a maximum value only after several explosions (compare Fig. 1), but decreases again when this is followed by several non-explosive reactions. The increased activity is due to the increased surface of the frozen reaction products, rather than to a specific chemical effect. An explosion gives rise to more finely divided products.

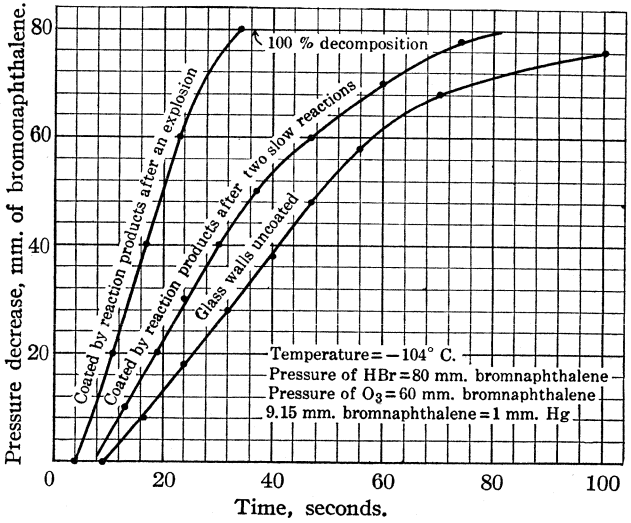


Fig. 1.—Influence of nature of surface on rate of reaction between hydrogen bromide and ozone.

Reaction rates for similar mixtures in a vessel having different activities are shown in Fig. 1. It can be shown that the straight-line portion is due to the lag in freezing out the reaction products and does not represent a zero order reaction. This is evident from Fig. 2, in which the rate is

[10] There are indications that when less ozone than half the hydrogen bromide pressure is used, somewhat more than two molecules of hydrogen bromide may be oxidized by one molecule of ozone but the results obtained so far are not quite conclusive. On the other hand, with excess ozone at higher pressures and especially at the higher temperature (−77°) it is possible that a small amount of ozone is decomposed in addition to that used to oxidize hydrogen bromide in accordance with the above equation.

[11] It is impossible to determine whether any or how much of the products are in the form of bromide hydrate.

much smaller for the lower pressures and the curves bend over earlier. If the reaction rates are compared, they are given very well by the relation

$$-\frac{\Delta p}{\Delta t} = k\,[\mathrm{HBr}]_{\mathrm{init.}}\,[\mathrm{O_3}]_{\mathrm{init.}} \qquad (2)$$

where $[\ ]_{\mathrm{init.}}$ represents the initial pressures. The k for several experiments is given in the last column of Table I.

TABLE I

THE INITIAL RATE OF THE REACTION BETWEEN HYDROGEN BROMIDE AND OZONE AT DIFFERENT CONCENTRATIONS

Temperature, −104°. Vessel uncoated. Pressure in mm. of bromonaphthalene

Pressure of HBr, mm.	Pressure of O_3, mm.	$-\frac{\Delta p_{\mathrm{mm.}}}{\Delta t_{\mathrm{sec.}}}$	$k = \frac{\Delta p_{\mathrm{mm.}}}{\Delta t_{\mathrm{sec.}}\,[\mathrm{HBr}]_{\mathrm{init.}}\,[\mathrm{O_3}]_{\mathrm{init.}}}$
80	84	1.43	0.021
80	58	1.25	.026
80	38	0.806	.026
60	48	.805	.028
38	44	.52	.031

The small but gradual change in the constants is due to a number of factors which can be shown to decrease the constants at the higher pressures.

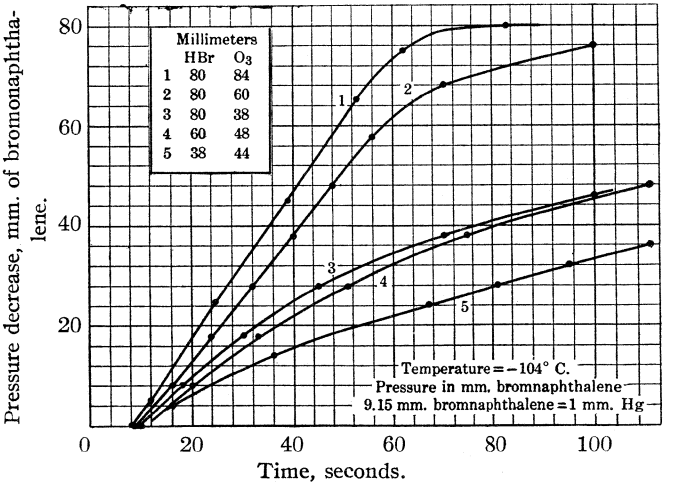


Fig. 2.—Rate of reaction between hydrogen bromide and ozone at different pressures in an uncoated vessel.

Relation (2) is valid in a vessel coated with the reaction products in which the rate of reaction is more than three times as fast as in the uncoated vessel.

From the average of experiments at −77°, k is found to be 0.125, whereas at −104° the average k is 0.026, both in an uncoated vessel. The temperature coefficient is therefore 1.79, which corresponds to a heat of activation of 3800 cal. in this temperature range.

The Effect of Surface and the Influence of Inert Gases on the Non-explosive Reaction.—In a vessel filled with small tubing the reaction was so rapid as to be complete in a few seconds at $-104°$. In vessels of different sizes with bare or coated walls, the surface, and therefore the activity, was not exactly reproducible. Therefore, no simple relationship could be found between the size of the vessel and the reaction rate. These experiments served, however, to provide additional evidence for the important role played by the surface in starting the reaction.

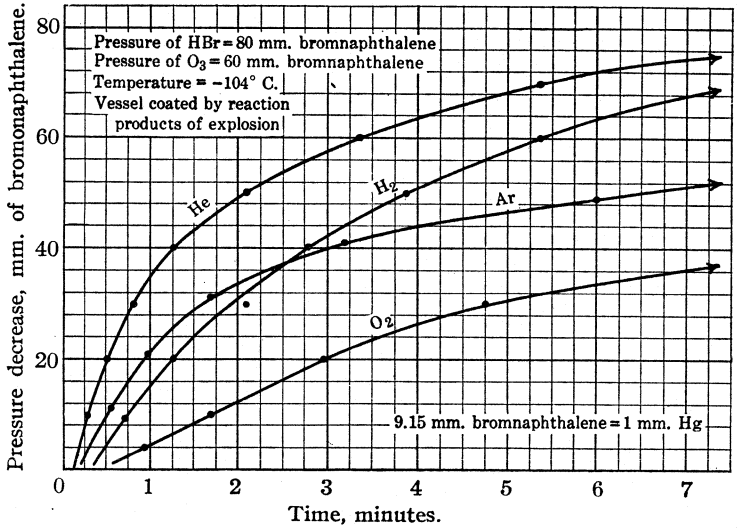


Fig. 3.—Influence of 300 millimeters of inert gas on rate of reaction between hydrogen bromide and ozone.

The rate of reaction decreases markedly with increasing amounts of inert gases. Table II gives the initial rate of pressure decrease for different pressures of four inert gases. The inhibiting influence increases in the order He, A, H_2,[12] O_2. To obtain a more complete picture of the inert gas effects, the curves in Fig. 3 are plotted. It is evident that the curve for argon intersects the curve for hydrogen and that for the latter gas the reaction is completed much earlier. It must be assumed that the inert gases influence only that part of the reaction taking place in the gas phase. It appears that the retarding influence of the inert gases is due to a combined effect of heat capacity and diffusibility. While the monatomic gases can remove less energy from the chain carriers than hydrogen and oxygen, the smaller rate of diffusion in argon begins to impede the reaction, especially at higher pressures, for the reacting gases close to the walls are

[12] Extended experiments with hydrogen indicate that it neither takes part in the reaction nor is acted upon by the reaction products, but that it behaves simply as an inert gas. See reference 6.

quickly used up and fresh gases find it more difficult to diffuse through argon than through hydrogen.

TABLE II

INFLUENCE OF INERT GASES ON THE REACTION BETWEEN HYDROGEN BROMIDE AND OZONE

Temperature, −104°. Vessel coated with reaction products from explosion. Pressure of HBr, 80 mm. of bromonaphthalene. Pressure of O_3, 60 mm. of bromonaphthalene.

Inert gas	$-\frac{\Delta p_{mm.}}{\Delta t_{sec.}}$ = the initial rate for the following inert gas pressures in mm. of bromonaphthalene			
	0	100	200	300
He	3.2	..	1.16	0.75
A	3.2	1.75	1.00	.58
H_2	3.2	1.47	0.68	.30
O_2	3.2	1.52	.50	.12

This marked influence of inert gases is in striking contrast to their slight effect on the ozone–bromine reaction, provided the explosion limit is not approached.[4]

The Explosion Limit.—The explosion limit studied here is what is usually known as the lower explosion limit. If an upper limit exists it cannot be measured conveniently. The transition from non-explosive to explosive reaction is a gradual one. As the pressure is raised, the reaction rate increases, until at the limit the reaction goes over into a general slow inflammation. In contrast with this a sharp detonation occurs if the pressure is raised still more—that is, about 1 mm. It is characterized by a loud click and instantaneous propagation of the explosion through the fine capillaries in the line.

The explosion limit depends on the pressures of both hydrogen bromide and ozone, but the influence of different factors on the explosion limit of equimolecular mixtures only were studied. The results obtained are similar to those found in the ozone–bromine reaction and are listed briefly.

1. The limit depends on the activity of the walls.

TABLE III

Conditions	Temp., °C.	Explosion limit, mm. of bromonaphthalene total pressure equimolecular mixture
Inactive vessel	−104	400
After several explosions	−104	340
Vessel coated with reaction products from previous explosion	−104	220
Active vessel (uncoated)	−104	340
Active vessel (uncoated)	− 77	340
Active vessel (uncoated)	0	160

2. No explosions could be obtained in a vessel filled with small glass tubing.

3. A hyperbolic relation was found between the explosion limit and the diameter of cylindrical vessels. Conclusions similar to those in the ozone–

bromine reaction may be drawn: namely, that it is necessary to build up a definite critical concentration of reaction carriers before an explosion results. The results show that the concentration of reaction carriers necessary to bring about an explosion is built up considerably faster in the ozone–hydrogen bromide reaction than in the ozone–bromine reaction.

Effect of Inert Gases on Explosion Limit.—Inert gases increase the explosion limit in the order A, O_2, He, H_2, which is the same order as in the ozone–bromine reaction.

Discussion

The experiments indicate clearly that the initial step in the reaction occurs at the walls between ozone and hydrogen bromide. Some active product, which we believe to be the OH radical, is ejected into the gas phase, where a series of reaction chains develops. The following mechanism is proposed to account for the experimental facts.

(1)	$HBr + O_3 = OH + O_2 + Br - 8$ Kcal.	Wall reaction
(2)	$OH + HBr = H_2O + Br + 30$ Kcal.	Gas phase reactions
(3a)	$H_2O^* + O_3 = O_3^* + H_2O$	
(b)	$H_2O^* + HBr = HBr^* + H_2O$	
(c)	$Br + Br + O_3 = Br_2 + O_3^*$	
(d)	$Br + Br + HBr = Br_2 + HBr^*$	
(4a)	$O_3^* + HBr = OH + O_2 + Br$	
(b)	$HBr^* + O_3 = OH + O_2 + Br$	

where the * indicates an energy-rich molecule.

From the temperature coefficient of the non-explosive reaction a heat of activation of 4000 cal. is found. This probably applies to the wall reaction 1. The calculation of the heat of reaction 1 gives −8000 cal. It is quite reasonable to assume that this value is reduced for the wall reaction to the 4000 cal. found by experiment. Activated O_3* or HBr* formed in 3a and b, c and d, may easily react in the gas phase as in 4a and b. The removal of bromine atoms by the reaction

$$Br + HBr \longrightarrow Br_2 + H$$

is improbable, since this reaction takes place with difficulty. A schematic diagram similar to that given in the ozone–bromine reaction[13] shows clearly how branching as well as straight chains may occur.

There are certain striking differences and similarities between the ozone–bromine and the ozone–hydrogen bromide reactions. The slight influence of inert gases in the non-explosive region on the former reaction and their large influence in the latter reaction, together with the fact that explosions are possible in the hydrogen bromide reaction in vessels of smaller diameter than with the ozone–bromine reaction, indicates that in the ozone–bromine reaction the number of reactions in a chain are relatively fewer and take place with difficulty (see also Ref. 4), whereas in the ozone–hydrogen bromide reaction the chains are long and occur with ease.

[13] Ref. 4, p. 2930.

The order of inert gases in increasing the explosion limit is exactly the same in the two reactions. On the other hand, the order of inert gases in their effect on the non-explosive reactions is different. For the explosion limits, the effectiveness of inert gases lies in their ability to transport to the wall the heat liberated in the fast reaction—that is, their heat conductivities. The higher the heat conductivity, the higher the explosion limit. However, in the non-explosive reaction the effectiveness of inert gases in decreasing the rate probably lies principally in their ability to deactivate carriers and terminate chains. There is no way of predicting the order, since it depends not only on the heat capacity of the inert gas but also on some specificity involving the transfer of energy from the particular carrier in each reaction to the inert gas molecule.

It is interesting that the non-explosive reaction follows the equation

$$2HBr + O_3 = H_2O + Br_2 + O_2$$

without further decomposition of ozone when it is present in excess. This is probably due to the fact that the energy taken up by ozone in 3a is insufficient to allow it to react with an ordinary ozone molecule (energy of activation *ca.* 29,000 cal.) but is sufficient for reaction 4a, which has a smaller energy of activation. The occurrence of a detonation at higher pressures and temperatures is probably due to the propagation of ozone chains.

The Effect of Hydrogen Chloride on the Ozone–Bromine Reaction and its Reaction with Ozone.—Since hydrogen chloride reacts readily with oxygen atoms,[7] this gas was used in an attempt to detect the presence of oxygen atoms in the decomposition of ozone sensitized by bromine. It was found that a very small amount, 0.5 mm., was sufficient to slow down the ozone decomposition very markedly and effectively to prevent an explosion at relatively high ozone pressures. The action of hydrogen chloride is obviously the same as that of water vapor—namely, it covers the walls and prevents the starting of reaction chains therefrom.

Larger amounts of hydrogen chloride undergo a very slow reaction with ozone at 0 and 25° which takes hours to complete itself in contrast to the few seconds necessary for the ozone–hydrogen bromide reaction. Chlorine is one of the products and probably also oxides of chlorine, which very likely react with the water to form acids. The reaction appears to be a wall reaction, but no chains are initiated in the gas phase due to unfavorable energy conditions. An extended study of this reaction was not thought profitable for our immediate purpose.

Summary

The kinetics of the non-explosive and explosive reactions between ozone and hydrogen bromide have been studied from 0 to −104°. *Inflammation and detonation have been observed down to −104°.* The de-

pendence of the rate of reaction and the explosion limit on size of vessel, activity of the wall, inert gases and temperature, have been investigated. The reaction affords another example in which *chains are initiated at the wall and are propagated thence into the gas phase.* In the proposed mechanism the OH radical is believed to be the carrier in these reaction chains.

The effect of hydrogen chloride on the bromine sensitized ozone decomposition and its reaction with ozone have been studied. Very small amounts of hydrogen chloride prevent explosions in the former, while its reaction with ozone seems to be confined to a wall reaction.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY THE IODINE–IODIDE COUPLE AT 25°

BY HERMAN A. LIEBHAFSKY

RECEIVED DECEMBER 7, 1931 PUBLISHED MAY 7, 1932

Introduction

The reaction system comprising hydrogen peroxide, iodine and iodide ion in neutral and dilute acid solutions has provided the material for a series of investigations extending over some three-fourths of a century, and culminating in the intensive work of Abel.[1] With the last of his papers on the subject, it seemed that these investigations could be regarded as complete, and that this reaction system, while apparently similar to the bromine–bromide system investigated by Bray and Livingston,[2] was in reality much more complex. In establishing a mechanism for this complex system, Abel deduced for the specific rate of the hydrolysis of iodine (into hypoiodous and hydriodic acids) a value which has proved irreconcilable with related experimental results.[3] The iodine–iodide reaction system is therefore being re-investigated over a wide range of experimental conditions: that part of the investigation dealing with the pure catalytic decomposition of hydrogen peroxide by the iodine–iodide couple is presented here.

Rate Measurements at the Steady State.—Within a short time after hydrogen peroxide is added to a netural solution of iodide ion, a *steady state* is reached, in which the main reaction is the catalytic decomposition of hydrogen peroxide

$$H_2O_2 = H_2O + {}^1/_2O_2 \qquad (1)$$

[1] (a) Abel, *Z. physik. Chem.*, **136**, 16 (1928); (b) *ibid.*, **96**, 1 (1920). For a comprehensive historical summary of earlier work by Abel and others, the reader is referred to Ref. 1b.

[2] Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923).

[3] (a) Liebhafsky, *Z. physik. Chem.*, **155**, 289 (1931); (b) THIS JOURNAL, **53**, 2074 (1931).

The establishing of this steady state is accompanied by an increase in the rate of oxygen evolution, which is initially zero, to the value determined at any temperature by the concentrations of the substances reacting at the steady state. After this rapid initial increase, the rate of oxygen evolution furnishes a convenient measure of the rate at which the catalysis, Reaction 1, proceeds. The results of a series of measurements show that the rate law for this evolution of oxygen[4] is

$$+\frac{dO_2}{dt} = kH_2O_2 \text{ or } -\frac{d(H_2O_2)}{dt} = k(H_2O_2) \qquad (2)$$

that is, the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple is always first order with respect to hydrogen peroxide.

The apparatus in Fig. 1 was patterned after that of Abel.[1b] The reaction mixture was stirred in a one-liter flask, indentations in which served as baffles. The evolved oxygen was measured in a gas buret attached to B; initial time was taken when the peroxide, added by inverting the cup A, hit the solution.

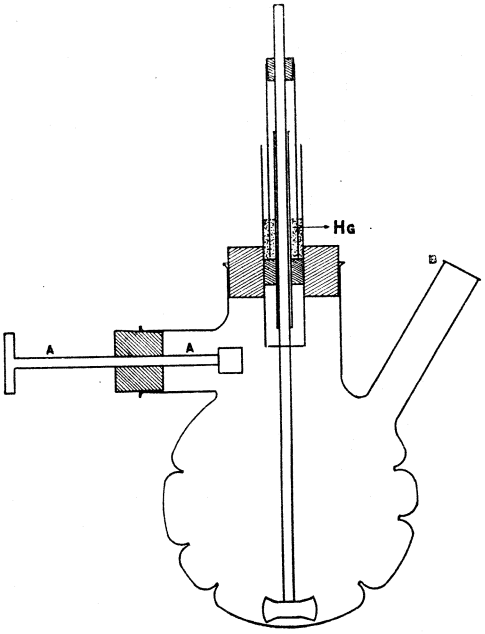


Fig. 1.—Gas evolution apparatus.

With a 400-cc. reaction mixture and moderate rates of oxygen evolution, the results depended on the rate of stirring only when this was below 900 r. p. m. When oxygen was evolved faster than 50 cc. per minute, as in experiments at high concentrations of iodide ion, where approximately half the peroxide decomposed in the first minute, accurate results were not obtained even with stirring above 1500 r. p. m.; irregularities in such results (*cf.* the right-hand side of Fig. 3) were attributed to supersaturation. For experiments at low (I^-), the addition of sand effectively prevented supersaturation.

For measurements at (I^-) below 10^{-2} *M* (*cf.* the left-hand side of Fig. 3) an accurate value for the rate of oxygen evolution was obtained before

[4] Since Equation 2 expresses the rate law for a first-order reaction, the value of k is independent of mass units, provided the same unit is employed throughout. k has therefore the same value in both the formulations given above. ( ) denotes "concentration of" in moles/liter; formulas alone denote quantities.

(H_2O_2) had sensibly changed, and k was taken as the quotient of this rate by the concentration of hydrogen peroxide. For experiments at higher (I^-) the following integral method was used in evaluating k. If x represents the cc. of oxygen evolved in such an experiment at an arbitrary time, t, and a represents the value of x when the reaction has gone to completion, then $k/2.30$ is the slope of the line obtained by plotting $a - x$ as ordinate on *semi-logarithmic* paper against t as abscissa. To illustrate this method of plotting and to demonstrate that Reaction 1 is first order with respect to hydrogen peroxide, the results of several experiments are given in Fig. 2.[5] Initial time is placed farther to the right for each experiment in order to prevent crowding.

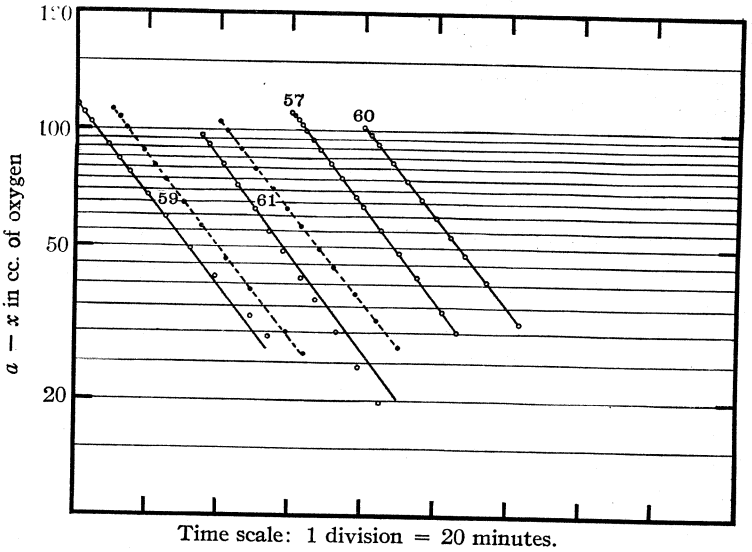


Fig. 2.—Typical rate experiments. (The plot is on semi-logarithmic paper. k values from these experiments are plotted on Curve II, Fig. 4.)

In Fig. 2, two experiments (Nos. 57 and 60) obey perfectly the first order rate law (Equation 2); the points of No. 61 show a downward, and those of No. 59 an upward, trend as the reaction nears completion. When the a values for these two experiments are properly corrected by the number of cc. of oxygen corresponding to the distance of the last point from the solid line, (for No. 61 a is increased by 8 cc., while for No. 59 a is decreased by 3 cc.) these trends disappear entirely as the broken lines,

[5] It may be pointed out here that the validity of Equation 2 is a sufficient proof that Reaction 1 is the main reaction taking place in the system, for Equation 2 shows that no substance in the system except hydrogen peroxide undergoes a concentration change in the course of the reaction, and it is stoichiometrically impossible to have this condition fulfilled and produce oxygen from hydrogen peroxide except by Reaction 1.

which have been plotted using the corrected a values, show. Such corrections eliminated both positive and negative trends, and, in general, left the value of k practically unaltered. Deviations from Equation 2 were therefore regarded as due only to errors in the experimentally measured value of a caused, for example, by a change in room temperature during the course of an experiment. Measurements were suspended in the slower experiments when these were approximately three-fourths complete, but more rapid experiments often showed Equation 2 to be obeyed within several per cent. of completion.

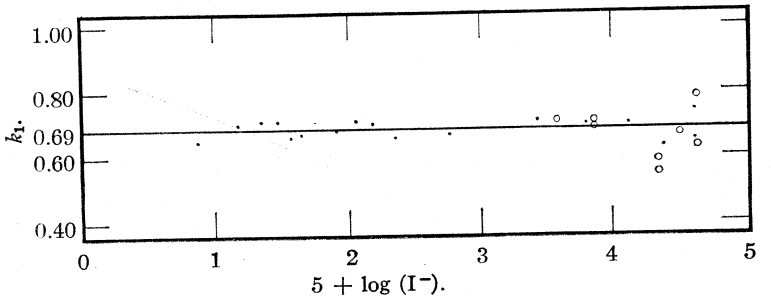


Fig. 3.—Summary of rate measurements in initially neutral iodide solutions: •, KI solutions; ⊙, NaI solutions.

From the results of previous investigations[1b,6] it was expected that in (nearly) neutral solution the complete differential equation for the rate at which hydrogen peroxide is catalytically decomposed would be

$$-\frac{d(H_2O_2)}{dt} = k'(H_2O_2)(I^-) \qquad (3)$$

corresponding to the reaction

$$H_2O_2 + I^- \xrightarrow{k_1} IO^- + H_2O \qquad (4)$$

by which hydrogen peroxide is reduced at the steady state. Since one mole of hydrogen peroxide is oxidized for every mole thus reduced, then, for the same concentrations of peroxide and iodide ion, $-(d(H_2O_2)/dt)$ in Equation 3 will be twice as great as $-(d(H_2O_2)/dt)$ for Reaction 4 at a distance from the steady state. It follows, therefore, that k' will be twice k_1, the specific rate constant for Reaction 4; or

$$k_1 = \frac{k'}{2} = \frac{k}{2(I^-)} \qquad (5)$$

The rate at which hydrogen peroxide is reduced at the steady state by iodide ion may now be written as

$$-\frac{d(H_2O_2)}{dt} = k_1(H_2O_2)(I^-) \qquad (6)$$

[6] (a) Among others, Walton, *Z. physik. Chem.*, **47**, 185 (1904); (b) Noyes, *ibid.*, **18**, 118 (1895).

The k_1 values plotted in Fig. 3 against log $(I^-) + 5$ as abscissa were obtained at 25° from measurements on a series of initially neutral reaction mixtures; the constancy of k_1 means that Reaction 4 is subject to practically zero salt effect when (I^-) is below 0.1 M and the ionic strength of the reaction system is at a minimum. That this is no longer true when foreign salts are present will be apparent from the k_1 values given in a later section (*cf.* Fig. 4). The value $k_1 = 0.69$ is in almost perfect agreement with the value $1.34/2 = 0.67$, which was obtained by Walton (Ref. 6a, Table 6) from similar experiments over a much smaller concentration range. The

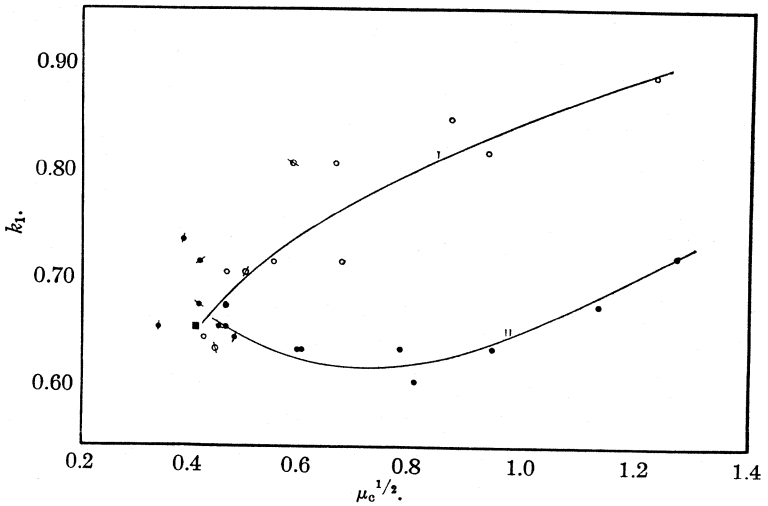


Fig. 4.—Variation of k_1 with ionic strength in the presence of Sörensen phosphate buffer. (Added salt: ○, $NaClO_4$ (Curve I); ●, Na_2SO_4 (Curve II); ϕ, KI, and ◐, phosphate buffer only. ■ is the initial point for Curves I and II, and corresponds to a reaction mixture in which $a_{H^+} = 1.01(10^{-7})$ and $(I^-) = 0.0215$).

value given by Abel for a reaction system containing acetate ion is somewhat higher (Ref. 1b, page 26, has $k_1 = 1.57/2 = 0.78$), probably mainly because the degree of dissociation of potassium iodide as obtained from conductivity measurements was used in its evaluation. Noyes[6b] finds, by following the rate of iodine formation in solutions of varying acid concentration, that $k_1 = 0.68$ to 0.82. Since this variation of k_1 is in the form of a trend with (H^+) which may be attributed (as Bray, *Z. physik. Chem.*, **54**, 463 (1906) has shown) to a third-order reaction

$$H_2O_2 + H^+ + I^- = HIO + H_2O$$

negligible in our reaction system, Noyes' value also is in good agreement with the result of the present investigation.

The theory of the hydrogen peroxide catalysis[1a,2] requires that there be, in addition to Reaction 4, a compensating reaction in which hydrogen per-

oxide is oxidized. The simplest one that has been suggested is the oxidation of H_2O_2 by IO^-, a product in Reaction 4

$$IO^- + H_2O_2 \longrightarrow I^- + H_2O_2 + O_2 \qquad (7)$$

Hypoiodite ion will exist in the reaction system at an extremely low concentration, always governed at the steady state by the equilibrium

$$I_2 + H_2O \rightleftharpoons IO^- + I^- + 2H^+ \qquad (8)$$

From Equations 7 and 8 it is apparent, therefore, that the absolute rate at which hydrogen peroxide is oxidized at the steady state may be written

$$-\frac{d(H_2O_2)}{dt} = k_2(IO^-)(H_2O_2) = k_2' \frac{(I_2)}{(I^-)(a_{H^+})^2\gamma_{I^-}\gamma_{IO^-}}(H_2O_2) \qquad (9)$$

In this expression k_2' is the product of k_2, the specific rate constant for Reaction 7, by K', the equilibrium constant for Reaction 8. Since no suitable values for the activity coefficients γ_{I^-} and γ_{IO^-} are available, Equation 9 will be written in the convenient form

$$-\frac{d(H_2O_2)}{dt} = k_2' \frac{(I_2)}{(I^-)(a_{H^+})^2}(H_2O_2) \qquad (9a)$$

We shall see later that the kinetic interpretation of our results does not depend upon this approximate formulation of Equation 9.

When the steady state has been reached, the rate at which hydrogen peroxide is reduced (Equation 3) is equal to the rate at which it is oxidized according to Equation 9a if *hypoiodite ion alone* oxidizes the peroxide. Subject to this condition, we may write

$$k_1(H_2O_2)(I^-) = k_2' \frac{(I_2)}{(I^-)(a_{H^+})^2}(H_2O_2) \qquad (10)$$

and

$$\frac{k_2'}{k_1} = \frac{(I^-)^2(a_{H^+})^2}{(I_2)} = F \qquad (11)$$

A sufficient constancy of F over a wide range of experimental conditions may thus serve as a test for the assumption that hydrogen peroxide is oxidized by hypoiodite ion alone. It may be pointed out here that F has the form of the steady state function found by Bray and Livingston for the bromine–bromide catalysis[7] where the hypohalous acid, and not the corresponding ion, was involved in both compensating reactions.

Concentration Measurements at the Steady State.—When hydrogen peroxide is added to an initially neutral solution of iodide ion, the approach to the steady state is characterized by the oxidation of a small amount of iodide according to the stoichiometric equation

$$3I^- + H_2O_2 = I_3^- + 2OH^- \qquad (12)$$

consequently, the solution becomes slightly alkaline. The accurate determination of F is most conveniently accomplished with the use of buffer

[7] *Cf.* Ref 2, p. 1262.

solutions, for then the activity of hydrogen ion at the steady state can be calculated with some degree of accuracy. When the initial concentration, $(I^-)_i$, of iodide ion in a reaction mixture at the steady state is known, and the total amount of oxidized iodide, $\Sigma(I_2)$, $\Sigma(I_2) = (I_2) + (I_2^-)$ has been determined by titration, the value of F may be calculated. In making this calculation, the equilibrium

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (13)$$

must be considered; $(I_2)(I^-)/(I_3^-) = 0.00140$ at 25°[8] was employed throughout in calculating (I_2) and (I^-). Any change of buffer in the approach to the steady state is, of course, governed by stoichiometric relations similar to those in Equation 12; the hydrogen ion activity used in the calculation of F was always that corresponding to the buffer solution actually present at the steady state.

For most experiments $\Sigma(I_2)$ was determined by titration with thiosulfate after all of the peroxide had been decomposed. For experiments in which this decomposition was very slow, however, it was often necessary to titrate while peroxide was still present: this could be accomplished satisfactorily when both (H_2O_2) and (I^-) were so low that no appreciable oxidation of iodide ion took place during titration. Such oxidation could always be detected by an "afterbluing" of the solution when the starch endpoint had once been reached. At these low concentrations of hydrogen peroxide, blank experiments showed no evidence of reaction between the peroxide and thiosulfate. In general, sufficient (two or more) determinations to ensure a reliable value of $\Sigma(I_2)$ were made for each steady state mixture.

The results of three series of such experiments are listed in Table I in which all data except the initial concentrations of iodide ion, $(I^-)_i$, are for the steady state. The values of a_{H^+} for Table Ia were obtained from the expression

$$P_H = -\log a_{H^+} = 4.73 + \log \frac{\text{acetate ion}}{\text{acetic acid}} + \log \gamma \qquad (14)$$

given by Cohn, Heyroth and Menkin;[9] the γ values given by the authors for buffer solutions M in total acetate and containing no other salt were employed in the calculation. In Table Ib,[10] values of a_{H^+} were calculated

[8] Jones and Kaplan, THIS JOURNAL, **50**, 1485 (1928).

[9] Cohn, Heyroth and Menkin, (a) *ibid.*, **50**, 696 (1928); (b) *ibid.*, **49**, 173 (1927).

[10] The experiments in Table Ib were carried out after a similar series, which is not published, to conserve space, employing Sörensen's phosphate solutions (see Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1928, p. 210) had been completed; values of F calculated from the latter varied from 0.8 (10^{-12}) to 1.8 (10^{-12}), and showed a positive trend with increasing (I^-). These variations were probably due in part to uncertainties in the calculated values of a_{H^+}, for with the Sörensen buffer (in which total phosphate is only 1/15 M) large changes in a_{H^+} often took place in the approach to the steady state.

from the apparent dissociation constants given by Cohn (Ref. 9b, Table VI); the effect of added salt on the buffer was again neglected. For experiments with a_{H^+} below 10^{-4} M, the values of F in Table I show no systematic variation with the concentration of any substance; indeed, all these values (except the first two in Table Ib, which are inaccurate)

TABLE I

CONCENTRATION MEASUREMENTS AT THE STEADY STATE[a]

(a) Measurements in Acetic Acid–Acetate Ion Buffer Solution (Total Acetate is 1 M)

Expt.	$a_{H^+}(10^5)$	$(I^-)_i(10^2)$	$(I_2)(10^3)$	$(I^-)(10^2)$	$(I_2)(10^4)$	$F = \frac{(a_{H^+})^2(I^-)^2}{(I_2)}(10^{12})$	μc
88	0.200	3.12	5.65	1.47	4.91	1.8	0.93
92	.234	0.780	0.576	0.622	1.01	2.1	.91
93	.39	.780	.835	.546	1.71	2.7	.86
89	.57	.780	1.060	.486	2.37	3.2	.81
90	1.01	.780	1.495	.372	4.08	3.5	.71
91	1.62	.234	0.352	.145	1.73	3.2	.60
87	2.50	.0780	.084	.059	0.59	[3.7]	.50
95	3.80	.390	1.092	.121	5.85	3.6	.40
96	6.00	.390	1.275	.087	7.87	3.5	.30
97	10.3	.390	1.438	.0590	10.1	3.6	.20
110	10.3	.388	1.442	.0580	10.2	3.5	.20
123	10.3	.388	1.424	.0600	9.95	3.8	.20
111	14.4	.388	1.504	.0480	11.25	4.3	.15
124	14.4	.388	1.509	.0475	11.25	4.2	.15
112, 125	22.6	.388	1.603	.0350	12.85	4.9	.10

[a] Inaccurate values are enclosed in brackets. All measurements were carried out at 25°. KI and KI_3 were considered as completely ionized.

(b) Measurements in Potassium Phosphate Buffer Solutions (Total Phosphate is 0.2 M)

Expt.	$a_{H^+}(10^7)$	$(I^-)_i(10^2)$	$\Sigma(I_2)(10^3)$	$(I^-)(10^2)$	$(I_2)(10^4)$	$F = \frac{(a_{H^+})^2(I^-)^2}{(I_2)}(10^{12})$
152	19.0	0.187	0.0052	0.186	0.022	[6]
153	19.0	.124	.0018	.123	.0096	[6]
155	16.3	1.56	1.36	1.29	1.33	3.3
150	2.06	1.56	0.050	1.55	0.041	2.5
159	2.05	3.12	.36	3.11	.155	2.6
149	1.98	4.68	1.02	4.39	.314	2.4
148	1.82	7.80	3.20	6.85	.64	2.4
145	1.71	12.58	9.69	10.66	1.26	2.6
146	1.42	23.40	33.4	18.25	2.54	2.6
151	1.37	15.4	10.0	12.4	1.11	2.6
147	0.694	Iodine added initially	144.2	49.0	4.11	2.8
158	.218	15.4	0.40	15.3	0.036	3.1
157	.171	31.2	2.17	31.1	.097	2.9
160	.114	Iodine added initially	13.89	78.2	.248	3.2
156	.078	78.0	6.26	76.1	.115	3.1

remain within a two-fold range while the product $(a_{H^+})^2\ (I^-)^2$ varies 10^{12}-fold: under these experimental conditions, therefore, the assumption that *hypoiodite ion alone* oxidizes hydrogen peroxide appears justified.

In interpreting the experiments for which a_{H^+} is greater than 10^{-4}, we must remember that from No. 89 to No. 123, Table Ia,[11] the value $F = 3.5\ (10^{-12})$ has been fairly well maintained despite a variation in the ionic strength, μ_c, from 0.81 to 0.20. That the increase in the values of F for the last four experiments might be due to a change in the ionic strength thus seems extremely improbable; consequently this variation will be treated as possessing a kinetic significance. The experimental data in Table Ia may, for the purpose of deducing a mechanism, be represented by the equation

$$F = 3.5(10^{-12}) + 1(10^{-8})(a_{H^+}) \qquad (15)$$

which will give the value of F in acetate buffer solution when the concentration of acetate ion is not above 0.8 M and no other electrolyte is present at high concentration. The first term is probably accurate to $\pm 5\%$, but the second must be regarded as an approximate upper limit only. Equation 15 is to be compared with the equation

$$F = 1.4(10^{-12}) + 1.3(10^{-7})(H^+) \text{ at } \mu_c = 0.4 \qquad (16)$$

which Abel obtained from similar experimental results in the region of hydrogen-ion concentrations $2(10^{-5})$–$2(10^{-7})$ M. The first six experiments of Table Ia lie in this region of acid concentrations; the F_A values calculated for these experiments by the substitution of their a_{H^+} values for (H^+) in Equation 16 are in substantial agreement with the F values of Table Ia. For the remaining experiments in the table, however, F_A thus calculated becomes increasingly larger than F as a_{H^+} increases, until for Experiments 112 and 125 F_A is over *six* times as large as the value $F = 4.8(10^{-12})$ experimentally obtained.[12]

[11] Certain of the experiments at the three highest values of a_{H^+} in Table I showed a pronounced decrease in $\Sigma(I_2)$ several hours after the steady state had been reached; to determine whether this decrease might be justifiably interpreted as an *increase* in F with increasing a_{H^+}, several reaction mixtures were prepared by adding hydrogen peroxide to the acetate buffer solution in equilibrium with finely divided iodine. For these reaction mixtures $(I_2) = 0.00132\ M$, and $(I^-) = (0.00140/0.00132)[\Sigma(I_2) - 0.00132]$. A decrease in $\Sigma(I_2)$ therefore means a decrease in (I^-); and, since a_{H^+} and (I_2) are constant, a decrease in F as well. Since such decreases were observed, this disappearance of iodine must be due to a factor not properly a part of the iodine–iodide system. Subsequent analyses proved the iodine to have been oxidized; it would seem, therefore, that the oxidation of iodine to iodate ion by hydrogen peroxide proceeds at lower values of (H^+) and with shorter induction periods when acetic, instead of perchloric (*cf.* Ref. 3b, Table V; these perchloric acid solutions were not buffered) acid is used. It may be worth pointing out, finally, that the occurrence of this oxidation was quite erratic, and that Table I contains for every value of a_{H^+} at least one experiment in which no such oxidation took place.

[12] See Ref. 1a. Abel calculated (H^+) from the dissociation constant for acetic acid; the concentration of acetate ion in his system was for most experiments 0.4 M.

To show, as Abel[1a] has already done, that the second term of Equation 15 may be attributed to the oxidation of hydrogen peroxide by hypoiodous acid, we need only to trace backward the reasoning by which Equation 11 was obtained. The steady state function corresponding to this term may obviously be written

$$F' = \frac{(a_{H^+})(I^-)^2}{(I_2)} = \frac{\kappa_2}{k_1} = 1(10^{-8}) \qquad (17)$$

The concentration of hypoiodous acid at the steady state is governed by the equilibrium

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \qquad (18)$$

and hence the rate law for the reaction

$$HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2 \qquad (19)$$

may be given the form (*cf.* Equations 9 and 9a)

$$-\frac{d(H_2O_2)}{dt} = \kappa_2(HIO)(H_2O_2) = \kappa_2'\frac{(I_2)}{(a_{H^+})(I^-)}(H_2O_2) \qquad (20)$$

κ_2', thus defined is the product of κ_2, the specific rate constant for Reaction 19 by K, the equilibrium constant for Reaction 18.

The values $K = 3(10^{-13})$,[13] $K' = 6(10^{-24})$[14] and $k_1 = 0.69$ will now be used to calculate k_2, the specific rate of Reaction 7, and the order of magnitude of κ_2. For 25° we obtain

$$k_2 = \frac{Fk_1}{K'} = 4(10^{11})$$

and

$$\kappa_2 = \frac{F'k_1}{K} < 2(10^4)$$

These values of k_2 and κ_2, deduced from Equation 15, naturally differ from those ((10^{11}) and $3.3(10^5)$, respectively) similarly deduced by Abel from Equation 16.[1a] Measurements of Reactions 7 and 19 at a distance from the steady state have been undertaken in this Laboratory in the hope that these may confirm the value of k_2, and establish more accurately the value of κ_2.

Effect on the Reaction System of Changing the Ionic Strength.—In Fig. 4 data are given to show the effect on k_1 of changing μ_c, the ionic strength expressed in moles/liter, by adding various salts. Curve I ($NaClO_4$) and Curve II (Na_2SO_4) both embody the results of two independent series of experiments on reaction mixtures of the composition given below Fig. 4, and to which known amounts of the proper salt were suc-

[13] Bray and Connolly, THIS JOURNAL, **33**, 1485 (1911).

[14] K' is obviously the product of K by the dissociation constant of HIO. The value

$$\frac{(H^+)(IO^-)}{(HIO)} = 2(10^{-11}) - 3(10^{-11})$$

is given by Fürth, *Z. Elektrochem.*, **28**, 57 (1922). We shall take $K' = 3(10^{-13}) \times 2(10^{-11}) = 6(10^{-24})$.

cessively added. Of the potassium iodide points, only those corresponding to the lower iodide concentrations are thoroughly reliable because of inaccuracies previously mentioned (*cf.* Fig. 3). The points in which only the phosphate buffer was changed (total phosphate is always 1/15 *M*) show a marked salt effect for a relatively small change in μ_c; in interpreting these data, it is important to remember that the most basic buffer mixture, which is almost pure Na_2HPO_4 solution, has a value of μ_c not very much greater than the most acid mixture, which is almost pure KH_2PO_4 solution. The phosphate points therefore represent the superposition of two salt effects, one for each type of phosphate. All the results of Fig. 4 may be summarized in the statement that the separate addition of various salts to the reaction mixture produces on k_1 effects which are in general small, not "linear" (*cf.* Ref. 16), and quite specific.

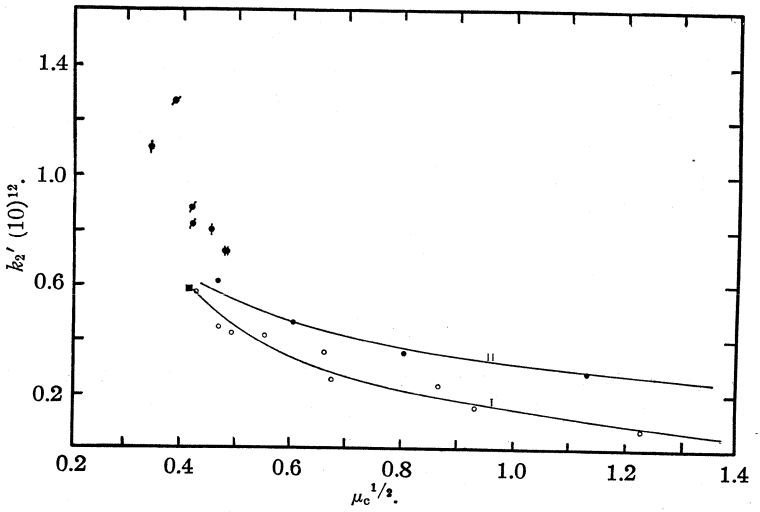


Fig. 5.—Variation of k_2' with ionic strength in the presence of Sörensen phosphate buffer. (Added salt: ○, $NaClO_4$ (Curve I); ●, Na_2SO_4 (Curve II); and ◐, phosphate buffer only. For composition of reaction mixture designated by ■, the initial point for the curves, see Fig. 4.)

An examination of Fig. 5 will reveal that addition of sodium perchlorate (Curve I) or sodium sulfate (Curve II) decreases the value of k_2' as calculated from the values of F and k_1 for each reaction mixture. It is apparent from Equation 9, which serves to define k_2', that this constant is more complex in nature than k_1, the specific rate of the simple bimolecular Reaction 4. As in Fig. 4, the phosphate points represent the superposition of two salt effects. No matter what salt is added, the effect on k_2' is relatively much greater than the corresponding effect shown in Fig. 4 for k_1; this result might have been expected from the fact that the concentra-

tion of hypoiodite ion is governed by the equilibria, Reactions 8 and 13, and by the buffer equilibrium which regulates the activity of hydrogen ion. The salt effect on k_2' is thus the resultant of several equilibrium salt effects,[15] which may be large, and a kinetic salt effect, which is probably small.

Jones and Kaplan have observed $(I^-)(I_2)/(I_3^-)$ to be constant for values of (I^-) below 0.3 M in solutions not saturated with iodine, and this constancy may be regarded as evidence that γ_{I^-} and $\gamma_{I_3^-}$ remain proportional to each other over this concentration range. It seems probable that this proportionality will be maintained when other salts are added in moderate amount to dilute solutions of tri-iodide ion—in other words, that our use of the value $(I^-)(I_2)/(I_3^-) = 0.00140$ at varying ionic strength is justified, and that Reaction 13 undergoes no salt effect as large as those in Fig. 5.

To determine whether these effects are due mainly to a salt effect on the equilibrium

$$H_2PO_4^- \rightleftharpoons HPO_4^{--} + H^+$$

measurements were made with a glass electrode of the hydrogen-ion activity in an equimolal Sörensen phosphate buffer solution to which other salts had been added. It was found that a_{H^+} was increased when μ_c was raised to 1 M by the addition of sodium perchlorate or sodium sulfate; the increase was greater for the perchlorate, but in both cases it was more than sufficient to explain any decrease in k_2' given by Curves I and II.

Finally, we shall consider how far our main conclusions are dependent on the empirical (and somewhat arbitrary) manner in which we have disposed of activity coefficients in the formulation of F (*cf.* Equations 9, 9a and 11). This formulation is convenient for three reasons: it employs the activity of hydrogen ion,[16] which, rather than the concentration, is given by buffer tables; it makes no assumption with regard to γ_{I^-} and γ_{IO^-}; and it is applicable to both the buffers employed. This formulation does assume, however, that substances present in the reaction system, but not properly a part of the buffer solution, do not affect the value of a_{H^+} given by the buffer tables. We have seen in the case of the phosphate

[15] Brönsted has given the name "secondary kinetic salt effect" to the salt effect on an equilibrium (see, for example, "The Velocity of Ionic Reactions," Contemporary Developments in Chemistry, Columbia University Press, 1927). The use of the term "equilibrium salt effect" might serve to distinguish more clearly between this and a true "kinetic salt effect," such as that on k_1, which has been called a "primary kinetic salt effect" by Brönsted.

[16] By "activity of hydrogen ion" in a solution is meant the quantity (whose negative logarithm may be regarded as the P_H of the solution) which may be obtained from a hydrogen electrode measurement. (In this connection, *cf.* Ref. 9a.) Whether an individual ion activity has an experimental significance in moderately concentrated solutions if the kinds and concentrations of other ions are left unspecified is another question.

buffer (*cf.* Fig. 5) that this assumption is not valid. In the case of the acetate buffer, however, the added iodide is so small (*cf.* Table Ia) that the value of a_{H^+} is probably unaffected by its addition. The conclusions drawn from Table Ia are therefore uncertain only to the extent to which changing (Ac^-) from 0.1 (Nos. 112, 125) to 0.9 *M* (No. 88) affects γ_{I^-} and γ_{IO^-}.

That this effect cannot be large enough to cause a mistake in the kinetic interpretation of the data is evident from the following considerations. If, in the thermodynamically exact formulation of *F*, the buffer equilibrium

$$HAc \rightleftharpoons H^+ + Ac^-$$

is included, Equation 11 becomes

$$F_{exact} = \frac{\gamma_I - \gamma_{IO} - (\gamma_{HAc})^2}{(\gamma_{Ac^-})^2 \gamma_{I_2}} \frac{(I^-)^2(HAc)^2}{(Ac^-)^2(I_2)} (K_{HAc})^2 \qquad (11a)$$

where K_{HAc} is the dissociation constant of acetic acid. Although the factor involving the activity coefficients is probably not equal to unity even in moderately dilute solutions, it is obvious that its value should change very little when the ionic strength is changed. This consideration leads to the very simple result that the concentration term, which we shall call F_c, in Equation 11a should be constant[17] for all experiments in Table Ia with a_{H^+} below 10^{-4} *M*. In Table II are listed values of F_c calculated for the experiments in Table Ia by use of the value $K'_{HAc} = 2.55$ (10^{-5})[18] for the buffer solution employed in Nos. 112 and 125, Table Ia.

TABLE II

RECALCULATION OF MEASUREMENTS IN TABLE Ia[a]

Expt.	112	124	123	96	95	87	91	90	89	93	92	88
	125	111	110									
			97									
(HAc)	90	85	80	70	60	50	40	30	20	15	10	8.8
(Ac^-)	10	15	20	30	40	50	60	70	80	85	90	91.2
F_c	5.0	4.2	3.6	3.4	3.6	3.8	3.5	4.0	4.0	3.5	3.1	2.7
F	4.9	4.3	3.6	3.5	3.6	3.7	3.2	3.5	3.2	2.7	2.1	1.8

[a] Average values are given for duplicate experiments.

The constancy of the F_c values is all that could be expected; at the higher acetate-ion concentrations they are more constant than the *F* values themselves. The approximate formulation of *F* in Equation 11

[17] Abel [*Z. physik. Chem.*, **122**, 49 (1926)] has pointed out that a similar simplification is possible in a study of the oxidation of iodide by iodate ion in acetic acid–acetate ion buffer solutions.

[18] Ref. 9a, Table II. The *apparent* dissociation constant is defined by the equation $K'_{HAc} = a_{H^+}(Ac^-)/(HAc)$; this value, rather than the *absolute* value $K_{HAc} = 1.86$ (10^{-5}), must be used if agreement with *F* as calculated for Nos. 112 and 125, Table Ia, is to be obtained. The use of the absolute value would not affect the above argument; for this relates only to the trend in F_c, which is unaffected by the value of K_{HAc} chosen.

therefore suffices for purposes of establishing a mechanism. A thermodynamically exact formulation of the steady state function cannot be given, however, until more knowledge is available regarding the activity coefficients concerned.

Conclusion

A re-investigation of the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple has confirmed the mechanism previously assigned to the decomposition at the steady state, and has demonstrated its validity over a much greater concentration range. Although the results obtained differ somewhat from those of Abel, these differences are not great enough to explain why his value for the specific rate of the iodine hydrolysis is smaller by several powers of ten than the lower limit deduced for this constant from related reaction systems. Preliminary experiments indicate that the solution of this difficulty may be found in the investigation of Reactions 7 and 19 at a distance from the steady state.

The author wishes to thank Mr. L. H. Donnally of this Laboratory for making the glass electrode measurements.

Summary

1. Measurements of the rate at which hydrogen peroxide is decomposed at 25° by the iodine–iodide couple yielded the value $k_1 = 0.69 \pm 3\%$ for the specific rate of the reaction

$$I^- + H_2O_2 \xrightarrow{k_1} IO^- + H_2O \qquad (4)$$

over a 10^3-fold range of iodide concentrations.

2. Subject to certain restrictions, the steady state function for this decomposition was found to be

$$F = 3.5(10^{-12}) + 1(10^{-8})a_{H^+} \text{ at } 25° \qquad (15)$$

3. By combining rate, steady state, and equilibrium data, the specific rates at 25° for the reactions

$$IO^- + H_2O_2 \xrightarrow{k_2} I^- + H_2O + O_2 \qquad (7)$$

and

$$HIO + H_2O_2 \xrightarrow{\kappa_2} H^+ + I^- + H_2O + O_2 \qquad (19)$$

were computed to be, respectively, $k_2 = 4(10^{11})$ and $\kappa_2 < 2(10^4)$. The value of κ_2 is much less accurate than that of k_2.

4. The reaction system has been studied over a series of ionic strength values produced by the addition of various salts.

5. For values of a_{H^+} below 10^{-4} M, only Reactions 4 and 7 need be assumed to explain the decomposition of hydrogen peroxide by the iodine–iodide couple at the steady state. As a_{H^+} is increased, Reaction 19 plays an increasingly important role; at the steady state, however, the absolute rate of Reaction 4 always equals the combined absolute rates of Reactions

7 and 19. This mechanism will explain the catalysis below the value of a_{H^+} at which oxidation of iodine by hydrogen peroxide begins.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA

BY EDWIN O. WIIG[1] AND G. B. KISTIAKOWSKY

RECEIVED DECEMBER 9, 1931 PUBLISHED MAY 7, 1932

The mechanism of the apparently simple photochemical decomposition of ammonia by ultraviolet light is still far from being settled. The reaction has been studied by Warburg and by Kuhn in light of wave length 2025–2140 Å. The former[2] obtained a quantum yield of 0.25, whereas the latter[3] found an average of 0.45 molecule of ammonia decomposed per quantum of light energy absorbed. In the far ultraviolet, 1600–1900 Å., the quantum yield reported by Kassel and Noyes[4] is 0.69 ± 0.24. These quantum yields have been calculated on the assumption that the photochemical decomposition follows the equation

$$2NH_3 = N_2 + 3H_2 \qquad (1)$$

However, Bates and Taylor[5] state that the products of decomposition contain 96% hydrogen and 4% nitrogen and express the view that hydrazine is formed, some of which may subsequently decompose. Recently, just as this work was completed, Koenig and Brings[6] reported hydrazine as a product of the photochemical decomposition of ammonia by ultraviolet light. By repeatedly flowing ammonia gas back and forth through a quartz vessel exposed to the radiation from a zinc spark for fifty hours and by continuously freezing out the hydrazine, a very minute quantity of the latter was condensed, sufficient for a qualitative test. Warburg and Kuhn determined the amount of reaction by measuring the increase in pressure, so that their low quantum yields might be accounted for by assuming that the reaction which occurs is largely

$$2NH_3 = N_2H_4 + H_2 \qquad (2)$$

instead of equation (1). Kuhn found that on complete decomposition of ammonia the pressure doubled; this, however, does not prove much since hydrazine would also decompose under such treatment.

It is evident then that the composition of the gas resulting from the photolysis of ammonia should be determined under the same conditions

[1] National Research Fellow in Chemistry.

[2] E. Warburg, *Sitzber. preuss. Akad.*, 746 (1911); 216 (1912).

[3] W. Kuhn, *J. chim. phys.*, **23**, 521 (1926); *Compt. rend.*, **177**, 956 (1923).

[4] L. S. Kassel and W. A. Noyes, Jr., THIS JOURNAL, **49**, 2495 (1927).

[5] J. R. Bates and H. S. Taylor, *ibid.*, **49**, 2438 (1927).

[6] A. Koenig and T. Brings, *Z. physik. Chem.*, Bodenstein Festband, 595 (1931).

that obtain during quantum yield measurements. It was the object of the present work to determine the nature of the gas formed when ammonia is exposed to ultraviolet light and to obtain the quantum yields for the reaction at room temperature and at higher temperatures.

Experimental Details

Light Source.—A condensed spark discharge served as the source of ultraviolet light. The spark gap was an adaptation of one described recently by Forbes and Brackett.[7] It consisted of two metallic disks 8 cm. in diameter and 5 mm. thick with V shaped edges. The disks—made of aluminum, zinc or cadmium—were mounted at right angles one above the other (Fig. 1) and were driven through reduction gears and insulated shafts by two Telechron clock motors. They revolved at the rate of one rotation in forty-five minutes, offering to the spark a steady supply of fresh surface and keeping its location sharply defined. The electrodes were connected, in parallel with a condenser,

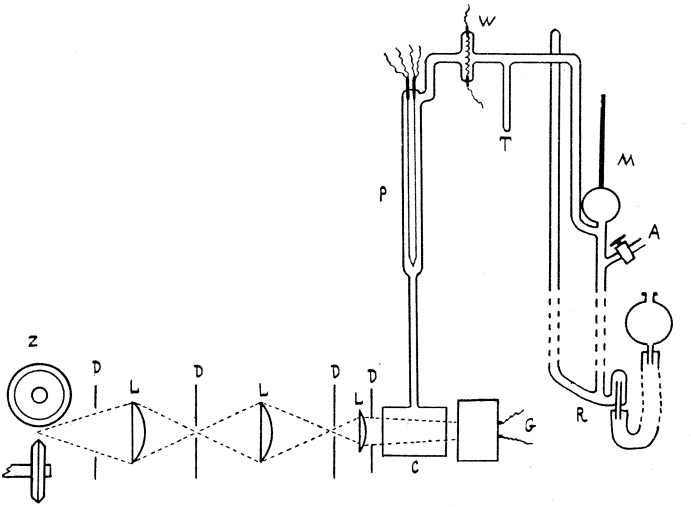


Fig. 1.—Apparatus: Z, spark electrodes; D, diaphragms; L, crystal quartz lenses; C, reaction cell; G, thermopile; P, Pirani gage; W, Pt wire for NH_3 decomposition; T, trap; M, McLeod gage; R, mercury manometer and leveling bulb; A, connection to the pump and gas storage bulbs.

to the poles of a 5 KVA, 10,000 v. transformer. A stream of air was blown across the spark gap. The arrangement worked very satisfactorily and the only source of complication was the home-made condenser, which heated gradually on continuous operation and caused a slow but steady decrease of light intensity.

The difficulty in obtaining large quartz prisms sufficiently transparent to wave lengths in the neighborhood of 2000 Å. led to the use of focal isolation instead of a monochromator in obtaining monochromatic radiation. The arrangement, shown schematically in Fig. 1, gave an approximately monochromatic beam, as shown by the fact that, according to thermopile measurements, as much as 95% of the radiation was ab-

[7] Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

sorbed by ammonia when zinc electrodes were used. Spectrograms of the light source confirmed this.

Apparatus and Materials.—The rate of ammonia decomposition was followed by measuring the pressure of hydrogen and nitrogen formed on freezing out ammonia. A McLeod gage and a Pirani gage were incorporated in the apparatus. By calibrating the latter with differently proportioned mixtures of nitrogen and hydrogen and by using both gages in each measurement, the possibility was given to determine not only the pressure but also the composition of the gases resulting from ammonia decomposition. The apparatus is shown schematically in Fig. 1. The quartz cell for the photolysis was of cylindrical shape, 50 mm. long and 25 mm. in diameter, with sealed polished windows. The McLeod gage was of usual construction and had a volume of *ca.* 150 cc. The Pirani gage consisted of 35 cm. of a platinum wire 0.076 mm. in diameter, suspended rigidly in the form of four loops in a 12 mm. tubing and silver soldered to platinum leads. The current through the gage was kept constant and the potential drop was measured by means of a Wolf potentiometer. The temperature of the wire was from 100 to 300° above the temperature of the surrounding constant-temperature (25.0°) water-bath. The gage was calibrated—using the McLeod gage of the system as standard—on carefully purified hydrogen admitted from a storage bulb and on a 1:3 nitrogen-hydrogen mixture prepared *in situ* by decomposing ammonia on the glowing platinum wire (Fig. 1). Tungsten wire was also used for this purpose with identical results.

The volume of the system was corrected for the effect of cooling the trap T (Fig. 1) in freezing out ammonia.

In high temperature experiments the quartz cell was wrapped with resistance wire and asbestos insulation. The temperature in these experiments was measured by a calibrated thermocouple in immediate contact with the quartz cell.

The source of ammonia gas was C. P. ammonium hydroxide solution contained in a storage flask connected with which was a tube of potash sticks and powdered sodium hydroxide, followed by a stopcock and suitable traps for condensing ammonia by cooling with liquid air. After freezing out the desired amount of ammonia with liquid air, the condensation bulb was surrounded with a carbon dioxide–acetone freezing mixture or a hydrochloric acid–ice mixture and the ammonia was allowed to distil into a second bulb surrounded by liquid air. A similar distillation from this bulb allowed the ammonia to expand into the reaction system. The first and last portions were discarded in each distillation.

Hydrogen bromide was prepared by dropping a C. P. 82% solution of hydrobromic acid on phosphorus pentoxide and passing the gas over red phosphorus and phosphorus pentoxide into a condensation bulb surrounded by carbon dioxide–acetone mixture and the hydrogen bromide was allowed to distil into a second bulb surrounded with liquid air. This was followed by a similar distillation into a third bulb from which another distillation sent the hydrogen bromide into a storage bulb connected with the pumping and reaction systems. The liquid hydrogen bromide in the last distillation was colorless.

The light energy was measured by means of a Moll "large surface" thermopile connected with a Leeds and Northrup galvanometer. A fixed diaphragm in front of the reaction cell, slightly smaller than the thermopile surface, aided in focusing the light on the pile. The galvanometer, thermopile and connecting wires were carefully shielded against electrical disturbances from the spark discharge. The calibration of the thermopile against a Bureau of Standards calibrated lamp was carried out exactly as recommended by the Bureau.

A typical experiment was carried out as follows. Ammonia was admitted into the reaction system, frozen in the trap T by means of liquid air and pumped until the pressure of any residual gases (on repeated evaporation and condensation of ammonia)

was less than 1×10^{-4} mm. The mercury leveling bulb was raised to fill the McLeod gage completely and the rubber tubing connecting the leveling bulb to the gage column clamped with a screw pinchcock. The stopcock shown in Fig. 1 prevented mercury from flowing into the main line of the pumping system. The liquid air was removed and the ammonia evaporated into the quartz cell and Pirani gage, its pressure being measured on a manometer sealed into the lower part of the McLeod gage column. After the decomposition, photochemical or thermal, the ammonia was frozen, evaporated and again frozen, the mercury leveling bulb lowered and the gaseous products allowed to expand into the McLeod gage, when the necessary readings on the gages were taken.

Experimental Results

Reaction Products.—The dependence of the quantum yield calculations on the nature of the products formed suggested the advisability of first investigating the composition of the gaseous products. Ammonia at pressures ranging from 13 to 377 mm. was exposed to the radiation of the zinc and aluminum sparks. Various lengths of illumination from one minute upward were employed, giving pressures of the products varying from 0.008 to 0.086 mm. Photochemical decompositions were alternated with thermal decompositions on the glowing wire. Three Pirani and three McLeod gage readings were taken alternately for each point. The results are shown in Fig. 2. Similar results were obtained in other series of experiments in which total radiation of the spark discharge was employed. The results show that the products of thermal and photochemical decompositions are identical. As it has been repeatedly shown that in the thermal decomposition a 1:3 nitrogen–hydrogen mixture is obtained, the same applies to the photochemical reaction. The limits of errors are difficult to estimate but the photochemical products contained certainly not more than 80 and not less than 70% hydrogen and in all probability were much nearer to the stoichiometric ratio.

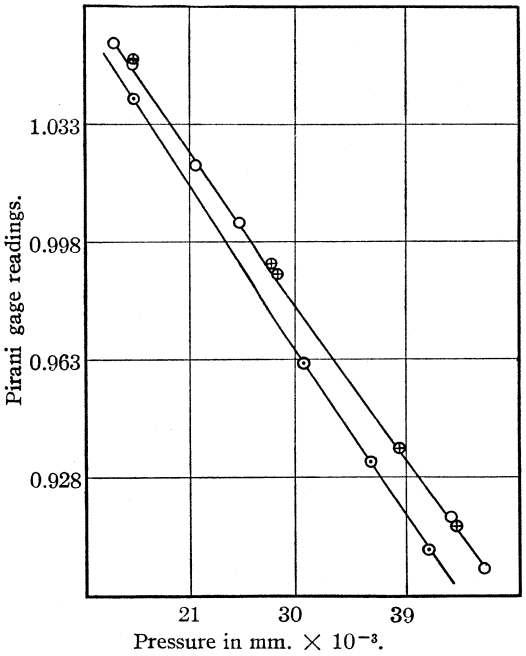


Fig. 2.—Pirani gage readings on the products of the thermal and photochemical decomposition of ammonia: ⊙, pure hydrogen; ○, products of thermal decomposition; ⊕, products of photochemical decomposition.

In some earlier series of these experiments the procedure in obtaining a 1:3 nitrogen hydrogen mixture was somewhat different. Ammonia was decomposed on the glowing wire to the extent of 0.2–0.3 mm. and the excess of decomposition products, on condensing ammonia, was pumped out until the desired pressure was obtained. Sometimes also a 1:3 mixture was admitted from a storage flask to a pressure of 0.2–0.3 mm. and later reduced by pumping. In all these experiments rather irregular results were obtained and it appeared that the products of photochemical decomposition contained more than 75% hydrogen. These results were

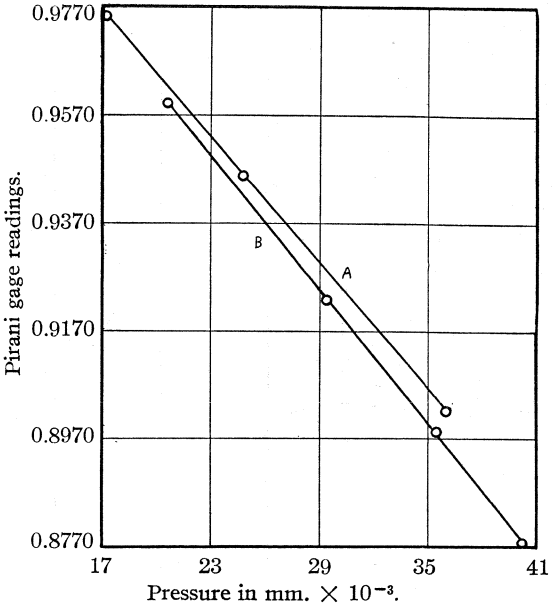


Fig. 3.—Comparison of methods of calibrating Pirani gage on $3H_2:1N_2$ mixtures: A, pressures reduced from 0.2 mm.; B, gas pressures produced by decomposition of NH_3 *in situ*.

ultimately traced to a partial separation of nitrogen and hydrogen while reducing their pressure by pumping. At the low pressures employed, hydrogen, due to its higher diffusion rate, is more rapidly removed from the system on opening the stopcock leading to the pumps than is nitrogen. As a result, the remaining mixture contains more than the original 25% nitrogen and a difference in composition is found in comparing the products of photochemical decomposition. The difficulty was avoided by decomposing ammonia on the glowing wire only until the desired pressure of nitrogen and hydrogen was obtained. All final results were obtained by this method. A comparison of the two methods is shown in Fig. 3.

Quantum Yields.—Ammonia was exposed for a period of ten to twenty minutes to the light obtained by focal isolation from the zinc, aluminum and cadmium sparks. The light energy was measured by means of the thermopile before and after the photolysis. Energy measurements were made with the quartz cell empty and filled with ammonia at the desired pressure, the difference giving the energy absorbed by the ammonia. Usually the intensity of the light source slowly decreased during an experiment. All experiments in which the energy absorbed by ammonia changed by more than 20% during the photolysis were discarded. The quantum yields rejected for this reason always agreed very well with those experiments in which the light source was more constant.

Occlusion of nitrogen and hydrogen by the solid ammonia would tend to give a low quantum yield. That no such occlusion occurred was shown in the following way. Ammonia at 25 mm. pressure was decomposed until the pressure of the products was 0.175 mm. Sufficient ammonia at high pressure, which had been carefully pumped until free of residual gases, was rapidly let into the reaction system. The total ammonia pressure was now 280 mm. and when this was frozen out the pressure of the nitrogen and hydrogen was again found to be 0.175 mm. A second experiment with the ammonia at pressures of 10 and 675 mm. gave 0.0239 and 0.0230 mm. of nitrogen and hydrogen, a change of less than 4% for a 67.5-fold increase in ammonia.

After the experiments were all completed, the rear window of the quartz reaction cell was cut away and, using the monochromatized light from the zinc spark, measurements were made of the energy falling on the thermopile without and with the rear window. The ratio of energy without to that with the window was 1.29. A similar quartz window on the thermopile was found to transmit 91.5% of the visible light with which the thermopile was calibrated and only 77.5% of the ultraviolet light falling on it. This gives a factor of 1.18 or a total factor of $1.18 \times 1.29 = 1.52$, by which the energy, as measured by the thermopile, is to be multiplied to obtain that reaching the ammonia within the cell.

Some doubts were felt concerning the accuracy of the absolute value of the quantum yields calculated by means of these corrections. They were based on the observation that the various parts of the thermopile surface differed in light sensitivity. With constant light intensity four equal areas gave mean galvanometer deflections of 2.23, 2.07, 2.68 and 3.32 cm., the first value being that obtained for the center section of the surface. The source of ultraviolet light was not homogeneous but appeared most intense at the center. Thus in our photochemical experiments the energy of the ultraviolet light falling on the thermopile was greater than that indicated by calibration against a uniform light source. Since the quantum yield for the decomposition of hydrogen bromide in the region with which

we are dealing is known to be 2.0,[8] it was decided to check our system on this substance.

Pure hydrogen bromide was admitted to the quartz cell and its photochemical decomposition followed exactly as in the case of ammonia. It was observed that hydrogen bromide underwent a slight thermal decomposition at room temperature. This slight reaction was determined before and after each photochemical decomposition and corrected for in calculating the quantum yield. In one experiment, for example, a total of 0.1142 mm. of hydrogen was evolved, while the correction amounted to 0.0026 mm. The average of the quantum yields found for hydrogen bromide, as shown in Table I, is 3.33 instead of the value of 2.0 found by Warburg. This latter value cannot be doubted. Not only is it the result of a very careful direct investigation, but it is also supported by numerous independent observations concerning the reactions of hydrogen and bromine atoms. Thus it must be concluded that the quantum yields for ammonia decomposition obtained by means of thermopile measurements must be further divided by 1.66. These corrected values are given in the following tables, II–V.

TABLE I

QUANTUM YIELDS FOR THE DECOMPOSITION OF HYDROGEN BROMIDE AT ROOM TEMPERATURE

Zn spark, mean λ = 2090 Å.

P_{HBr}, mm.	Time of illumination, sec.	P_{H_2}, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
38	983	0.0886	2951	3.77
37	917	.1016	4015	3.40
28	967	.1116	4033	3.53
20	831	.0941	4678	2.99
12	710	.0240	1400	2.98
			Mean	3.33

The quantum yields of the ammonia decomposition obtained at room temperatures (21–30°) are given in Tables II, III and IV. A typical experiment showed the following data and calculations:

Mean λ, 2090 Å.; apparent volume of system, 204 cc.; temp., 26.7°; NH_3, 110 mm.; galvanometer deflection of 1 cm. = 235.3 ergs/sec.; time of exposure, 1071 sec.; pressure ($N_2 + 3H_2$), 0.0692 mm.

At start of experiment { Av. galv. defl. without NH_3 in cell = 13.15 cm.
Av. galv. defl. with NH_3 in cell = 1.54 cm.

At end of experiment { Av. galv. defl. without NH_3 in cell = 12.55 cm.
Av. galv. defl. with NH_3 in cell = 1.31 cm.

$$\text{Mean energy absorbed by } NH_3 = \left[\frac{(13.15 - 1.54) + (12.55 - 1.31)}{2}\right] \times 235.3 \times 1.18 \times 1.29 = 4090 \text{ ergs/sec.}$$

Total energy absorbed by NH_3 = 466 × 10^{15} quanta

[8] E. Warburg, *Sitzb. preuss. Akad.*, 314 (1916).

$$\text{Molecules } NH_3 \text{ decomposed} = 6.06 \times 10^{23} \times \frac{204}{22{,}400} \times \frac{0.0692}{2 \times 760} \times \frac{273}{299.7} = \frac{229 \times 10^{15}}{}$$

$$\text{Apparent quantum yield} = \frac{229 \times 10^{15}}{466 \times 10^{15}} = 0.49 \text{ molecule/quanta}$$

$$\text{Corrected quantum yield} = \frac{0.49}{1.66} = 0.30 \text{ molecule/quanta}$$

TABLE II

QUANTUM YIELDS IN THE DECOMPOSITION OF AMMONIA AT ROOM TEMPERATURE

Zn spark, mean λ = 2090 Å.

P_{NH_3}, mm.	Time of illumination, sec.	$P_{H_2+N_2}$, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
815	780	0.0322	4506	0.17
630	751	.0371	5426	.17
630	758	.0330	5308	.15
515	1059	.0521	4843	.19
513	1354	.0713	4542	.22
239	779	.0459	4391	.26
228	771	.0384	4373	.22
219	891	.0207	1938	.22
111	879	.0514	4022	.27
111	786	.0534	4710	.27
111	812	.0581	4477	.30
110	1071	.0692	4090	.30
106	841	.0242	2532	.21
70	810	.0228	2428	.22
59	768	.0399	3736	.26
57	866	.0476	3489	.30
12	817	.0273	3087	.21
10	871	.0239	3055	.17
5	885	.0197	2314	.18
			Mean	.23

TABLE III

QUANTUM YIELDS IN THE DECOMPOSITION OF AMMONIA AT ROOM TEMPERATURE

Al spark, mean λ = 1962 Å.

P_{NH_3}, mm.	Time of illumination, sec.	$P_{H_2+N_2}$, mm.	Mean energy	Quantum yield, mole/quantum
430	814	0.0192	1931	0.24
430	1679	.0148	698	.25
225	1223	.0228	1479	.25
190	1122	.0256	1748	.26
110	1091	.0327	2081	.29
103	1407	.0388	1913	.29
51	1460	.0340	1941	.24
12	1419	.0267	1547	.24
4	1403	.0097	731	.19
4	1996	.0149	673	.22
1	2013	.0120	566	.21
			Mean	.24

TABLE IV

QUANTUM YIELDS IN THE DECOMPOSITION OF AMMONIA AT ROOM TEMPERATURE

Cd spark, mean λ = 2144 Å.

P_{NH_3}, mm.	Time of illumination, sec.	$P_{H_2+N_2}$, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
116	1427	0.0207	910	0.29
112	1131	.0177	1433	.20
109	1370	.0113	587	.26
				Mean .25

Kuhn[9] reported a nine-fold increase in quantum yield of ammonia decomposition on increasing the temperature from 20 to 500°. As Kuhn has not given any details of his measurements it seemed desirable to repeat his work, particularly since photographs of ammonia absorption spectra taken at high temperatures showed several new bands appearing in the region 2100–2500 Å. and those present at room temperature being enhanced. As measurements of light energy absorbed by ammonia at 500° offered considerable difficulties, the energy measurements were carried out at room temperature. The error thus introduced is negligibly small since with our monochromatizing system about 90% of energy is absorbed and, as photographs showed, absorption in this (2100 Å.) region increases with temperature. After determining the energy absorbed ammonia was frozen out, the cell quickly heated to the desired temperature and ammonia vaporized. After completion of illumination ammonia was frozen out again, the cell quickly cooled and a second measurement of absorbed light energy made. Before each experiment the cell was degassed at 500°.

In calculating the quantum yields given in Table V corrections have been made for ammonia decomposed while energy measurements were performed and for a very slight thermal decomposition in the cell at high temperatures.

TABLE V

QUANTUM YIELDS FOR THE DECOMPOSITION OF AMMONIA AT HIGH TEMPERATURES

Zn spark, mean λ = 2090 Å. Time of illumination, 600 sec.

Temp., °C.	P_{NH_3}, mm.	$P_{H_2+N_2}$, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
300	150	0.0200	1834	0.34
	95	.0328	2543	.40
				Mean .37
500	148	0.0511	3206	0.49
	142	.0397	2403	.50
	89	.0351	2314	.46
				Mean .48

The Reaction Mechanism.—The results here obtained may be summed up as follows. The gaseous products of decomposition are very nearly

[9] W. Kuhn, *Compt. rend.*, **178**, 708 (1924).

a 1:3 nitrogen–hydrogen mixture, irrespective of the time of illumination. The quantum yield is 0.25 at room temperature and about double this value at 500°. It does not depend on ammonia pressure over the range 800 to 1 mm., wave length of radiation from 2150 Å. to 1960 Å., intensity of radiation varied seven-fold and amount of decomposition varied seven-fold.

These results are in partial agreement with the data already recorded in the literature. From the description of Koenig and Brings[6] it is apparent that hydrazine is present only in traces even in rapidly flowing ammonia. Our results point in the same direction. Moreover, it is possible to show that low, if any, yield of hydrazine is not due to its secondary photochemical decomposition. Experiments of Elgin and Taylor[10] indicate that the photochemical decomposition of hydrazine has a quantum yield not much greater than unity. The absorption spectrum of hydrazine[11] is continuous and thus absorption certainly follows Beer's law. A rate of photochemical decomposition of hydrazine sufficiently rapid to explain our failure to detect this substance would require light absorption coefficients at least 10^5 higher than those of ammonia in the region 2150–1970 Å. From Elgin's qualitative description such large values seem to be out of the question.

Bates and Taylor assumed hydrazine formation, finding excess hydrogen in decomposition products of ammonia. Their experimental set-up favored, however, an accumulation of hydrogen, due to its rapid diffusion, in the analytical part of the apparatus. An effect of this type was discussed here on previous pages and Professor H. S. Taylor in a personal discussion suggested it as a possible explanation of his and Bates' results.

The results of Dickinson and Mitchell[11] which also indicate an excess of hydrogen in photochemical decomposition of ammonia are somewhat inconclusive as the authors themselves admit.

The value of the quantum yield here obtained agrees excellently with the value given by Warburg. In view of this agreement one may safely conclude that Kuhn's value is erroneous. Possibly the use of a surface thermopile without correcting it for unequal sensitivity caused an error similar to one described on previous pages. The pronounced decrease in the quantum yield, which Kuhn found on improving the monochromacy of radiation, is impossible to explain. It cannot be incorporated in any theory of the reaction which has been set up and we are inclined to attribute it to some unknown experimental error.

Kassel and Noyes[4] found a quantum yield about 0.69 in the spectral region 1600–1900 Å.

As the authors point out, this value may be somewhat too high. From

[10] Elgin and Taylor, THIS JOURNAL, **51**, 2059 (1929).

[11] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

kinetic considerations (see later) it seems more likely that with these short wave lengths the same quantum yield obtains as in the region above 1950 Å. However, an increase of quantum yield is not impossible from the point of view of the most likely reaction mechanism and only some future experiments can decide the correctness of Kassel and Noyes' value.

Kuhn[3] reported a nine-fold increase in quantum yield from 20 to 500°, while here only a doubling has been observed. In absence of any experimental details it is impossible to say whether Kuhn measured the quantum yield or only the reaction velocity at high temperatures and whether some light of wave lengths longer than 2100 Å. was present. In the latter case the change of ammonia absorption with temperature may partly account for Kuhn's results. On the other hand, in the present experiments the quartz cell may have been more opaque to radiation while heated to high temperatures. This is quite in accord with the generally observed shift of absorption to longer wave lengths in liquid and solid systems. Furthermore, some of the gas formed in ammonia decomposition may have been adsorbed on the walls of the quartz cell after cooling. Thus the doubling of quantum yield between room temperature and 500° appears rather as the lower limit of the temperature coefficient of the quantum yield.

As has been pointed out by Lind[12] the temperature coefficient observed by Kuhn is almost identical with the value found by Wourtzel[13] for the ammonia decomposition by α-particles.

This agreement undoubtedly supports Kuhn's value as contrasted with ours. For the following considerations the numerical value of the temperature coefficient is, however, not of paramount importance. Its existence shows the presence of some secondary reactions requiring activation energy and favoring the decomposition.

Further facts to be considered in setting up a mechanism of ammonia decomposition are that neither nitrogen nor hydrogen has any effect on reaction rate at room temperature[2,14] but that the latter retards the rate at 500°.[3]

Bonhoeffer and Farkas[15] have shown that ammonia is decomposed photochemically at pressures as low as 10^{-3} mm. This, together with the absence of rotational structure in absorption bands of ammonia and lack of fluorescence, led the authors to suggest that ammonia molecules decompose without intervention of collisions in a predissociation[16] process. The time interval between light absorption and dissociation in such proc-

[12] "Chemical Effects of α-Particles," Chemical Catalog Company, New York, 1928, p. 215.

[13] Wourtzel, *Le Radium*, **11**, 342 (1919).

[14] Coehn and Pringent, *Z. Elektrochem.*, **20**, 275 (1914).

[15] Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1928).

[16] V. Henri, "Structure des Molecules," Paris, 1925.

esses has been variously estimated as 10^{-10}–10^{-11} sec., thus a time comparable to average time between molecular collisions at atmospheric pressure. It is, however, necessary to assume that collisions have no effect on dissociation of excited ammonia molecules since otherwise a change of quantum yield with pressure would have been observed. Thus the deficiency of quantum yield must be due to some secondary reactions in which the dissociation products recombine again to form ammonia molecules. There are two energetically possible ways in which ammonia could decompose

$$\text{I} \quad NH_3 + h\nu \longrightarrow NH + H_2$$
$$\text{II} \quad NH_3 + h\nu \longrightarrow NH_2 + H$$

The first scheme leads however to reaction mechanisms which do not agree with experimental facts. The reaction $2NH \longrightarrow N_2 + H_2$ would give a quantum yield unity. The reaction $NH + H_2 \longrightarrow NH_3$ would require retardation by hydrogen. The reaction $NH + NH_3 \longrightarrow N_2H_4$ would result in a quantitative formation of hydrazine since no mechanism is available for its decomposition (the reaction $N_2H_4 + NH \longrightarrow NH_3 + N_2 + H_2$ would again give a quantum yield unity).

The second mode of decomposition has numerous observations in its favor.

Thus Farkas, Haber and Harteck[17] were able to sensitize hydrogen–oxygen and carbon monoxide–oxygen reactions by decomposing photochemically ammonia added to the gas mixtures. Taylor and Emeléus[18] sensitized in the same manner polymerization and hydrogenation of ethylene, while Hill and Vernon[18] reduced tungstic oxide by decomposing ammonia at low pressures. All these effects are interpreted as indicating the presence of hydrogen atoms.

The secondary reactions to be considered if ammonia decomposes according to the second scheme are

$$H + H + M \longrightarrow H_2 + M \quad (1)$$
$$NH_2 + H + M \longrightarrow NH_3 + M \quad (2)$$
$$NH_2 + H_2 \longrightarrow NH_3 + H \quad (3)$$
$$NH_3 + H \longrightarrow NH_2 + H_2 \quad (4)$$
$$NH_2 + NH_2 + M \longrightarrow N_2H_4 + M \quad (5)$$
$$NH_2 + NH_2 \longrightarrow N_2 + 2H_2 \quad (6)$$
$$N_2H_4 + H \longrightarrow N_2H_3 + H_2 \quad (7)$$
$$N_2H_3 + N_2H_3 \longrightarrow 2NH_3 + N_2 \quad (8)$$

For reactions 2 and 5 the triple collisions are not absolutely necessary on account of a larger number of internal degrees of freedom available, but are rather likely.

In considering the reaction mechanism at room temperature, reactions 3 and 4 may be neglected. The first would require a retardation by

[17] Farkas, Haber and Harteck, *Naturwissenschaften*, **12**, 267 (1930).

[18] Taylor and Emeléus, THIS JOURNAL, **53**, 562 (1931).

hydrogen; the second has been shown to occur extremely slowly by Boehm and Bonhoeffer.[19] For the decomposition at high temperatures, on the other hand, these reactions are probably quite important, the one producing the observed retardation by hydrogen, the other the increase of quantum yield.

The simplest scheme of secondary reactions at room temperature involves processes 1, 2, 6. It leads, however, to a quantum yield dependent on total pressure; since reaction 1 requires triple collisions, reaction 6 certainly does not, while 2 is doubtful. In the more general case, when it is assumed that reaction 2 requires triple collisions at low pressures but does not at high, a pronounced minimum of quantum yield would be obtained in the transition pressure region of reaction 2. This is certainly not the case experimentally since if anything a slight maximum was observed at intermediate pressures with zinc spark.

The remaining possibility involves reactions 1, 2, 5, 7, 8. The quantum yield is now determined by the ratio $\kappa_2^2/\kappa_1\kappa_5$ which must be equal to eight if the quantum yield is 0.25. Since it is quite possible that all these reactions require triple collisions, the quantum yield may be independent of pressure. It will be also independent of light intensity and amount of decomposition. Reaction 1 needs no further justification and reaction 2 is also quite likely to occur. Reaction 5 is made plausible by the finding of traces of hydrazine in ammonia decomposition experiments by the flow method.

Reactions 7 and 8,[20] necessary to explain the absence of larger amounts of hydrazine, may appear somewhat artificial. However, independent evidence can be adduced in their favor. Elgin and Taylor[10] found that in the presence of excited mercury the decomposition of hydrazine was about twice as fast as the rate of water formation. Using an incorrect value of Marshall[21] for the quantum yield of the latter reaction, they attempted to derive a chain mechanism for hydrazine decomposition. In the meantime Frankenburger and Klinkhard[22] have shown that water formation has a quantum yield near unity. Thus two molecules of hydrazine must be decomposed by each excited mercury atom. This finds a most simple explanation in the scheme

$$N_2H_4 + Hg^* \longrightarrow N_2H_3 + H + Hg$$
$$N_2H_4 + H \longrightarrow N_2H_3 + H_2$$
$$2N_2H_3 \longrightarrow 2NH_3 + N_2$$

The scheme accounts for the quantum yield, the nature of the reaction products and also for the observation of Elgin and Taylor that in presence

[19] Boehm and Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

[20] Reaction 8 could be replaced by $N_2H_3 + NH_2 \longrightarrow N_2 + H_2 + NH_3$. A decision is impossible at present.

[21] Marshall, *J. Phys. Chem.*, **30**, 1078 (1926).

[22] Frankenburger and Klinkhard, *Trans. Faraday Soc.*, 431 (1931).

of excess hydrogen the rate of hydrazine decomposition remains unchanged. In the latter case the primary reaction is $Hg^* + H_2 \longrightarrow Hg + 2H$ followed by the two last reactions of the preceding scheme. The reactivity of hydrogen atoms toward hydrazine and their inertia toward ammonia are quite analogous to their behavior toward methane and higher saturated hydrocarbons.[23]

Results obtained in the extensive work on electric discharges through ammonia and on allied phenomena are somewhat discordant and no binding conclusions can be drawn.

Steiner's[24] conclusion that in the reactions of atomic nitrogen and hydrogen hydrazine is formed by the reaction $2NH_2 + M \longrightarrow N_2H_4 + M$ agrees with the one proposed here. However, Steiner's conclusions should be reviewed in the light of the unquestionable fact that hydrogen atoms decompose hydrazine.

Koenig and Wagner[25] find that by decreasing electric current and increasing ammonia flow through silent discharges, the net reaction $2NH_3 \longrightarrow N_2H_4 + H_2$ can be made to occur almost quantitatively. A decomposition of ammonia by electron impact in the way suggested by the authors: $NH_3 \longrightarrow NH + H_2$, followed by the reaction $NH + NH_3 \longrightarrow N_2H_4$, accounts for these results much better than the decomposition $NH_3 \longrightarrow NH_2 + H$. In the latter case a quantitative yield of hydrazine could hardly be expected judging from the photochemical reaction.

Results which do not agree with the mechanism of ammonia decomposition proposed herein are contained in the work of Gedye and Allibone[26] on ammonia decomposition by high speed electrons. They find that the hydrazine yield increases with decreasing pressure in the range 700 to 50 mm. If NH_2 radicals are formed here, hydrazine formation is a triple collision process, the decomposition a bimolecular reaction and roughly a proportionality of the yield with pressure should be expected. Formation of NH radicals does not make the explanation simple either. The suggestion of the authors that hydrazine formation is a wall reaction would require an extraordinary chemical inertia of whatever radicals and atoms are formed, so that these have time to diffuse to the walls.

One difficulty of the proposed ammonia decomposition mechanism has not been touched upon yet. Accepting the velocity constant of hydrogen atom recombination as determined by Steiner and Wicke[27] or by Senftleben and Riechemeyer[28] it is found that reactions 1, 2, 5 must proceed chiefly in the gas phase near the upper limits of ammonia pressures here

[23] Bonhoeffer and Harteck, *Z. physik. Chem.*, **139,** 64 (1928).
[24] Steiner, *Z. Elektrochem.*, **36,** 807 (1930).
[25] Koenig and Wagner, *Z. physik. Chem.*, **144A,** 213 (1930).
[26] Gedye and Allibone, *Proc. Roy. Soc.* (London), **A130,** 346 (1931).
[27] Steiner and Wicke, *Z. physik. Chem.*, Bodenstein Festband, 817 (1931).
[28] Senftleben and Riechemeyer, *Ann. Physik,* **6,** 105 (1930).

investigated. Near the low limit of this pressure however the atoms and radicals have a 1000:1 chance to diffuse to the walls before reaction. Thus it becomes necessary to assume that the ratio $\kappa_2^2/\kappa_1\kappa_5$ is the same for wall and gas reactions.

While this new assumption is not very satisfactory, it offers at any rate new means of testing the theory by studying ammonia decomposition at low pressures in vessels with walls prepared either to accelerate or retard the hydrogen atom recombination. Such experiments are considered for the near future by one of us.

Concluding, we would like to thank Professor G. S. Forbes for his frequent help and the loan of some of the equipment used in this work.

Summary

1. The gaseous products of the photochemical ammonia decomposition are a 1:3 nitrogen–hydrogen mixture even under conditions excluding a photochemical decomposition of hydrazine.

2. The quantum yield of ammonia decomposition at room temperature is 0.25 independent of pressure, light intensity and time of illumination.

3. At 500° the quantum yield is 0.5 or more.

4. The bearing of these results on other work on ammonia decomposition is discussed and a mechanism of ammonia decomposition is developed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 90]

THE SORPTION OF GASES BY IRON

BY ARTHUR F. BENTON AND T. A. WHITE[1]

RECEIVED DECEMBER 12, 1931 PUBLISHED MAY 7, 1932

Introduction

As a result of numerous researches in recent years in the field of adsorption of gases by catalytically active solids, three processes, apart from compound formation, have become clearly recognized—physical adsorption, activated adsorption and solution. The characteristics and interrelationships of the two types of *ad*sorption are now reasonably clear.[2]

In the attempt to distinguish adsorption from solution, it has been customary to assume that the former is always rapid, while the latter is ordinarily slow. However, since it has been shown that activated ad-

[1] Du Pont Fellow in Chemistry.

[2] (a) Benton, THIS JOURNAL, **45**, 887, 900 (1923); (b) Benton and White, *ibid.*, **52**, 2325 (1930); (c) Taylor, *ibid.*, **53**, 578 (1931); (d) Taylor and Williamson, *ibid.*, **53**, 2168 (1931); (e) Taylor and McKinney, *ibid.*, **53**, 3604 (1931); (f) Benton and White, *ibid.*, **54**, 1373 (1932).

sorption may be a slow process,[2b-f,3] it is clear that rate alone is not a certain criterion. Nevertheless, in the systems copper–hydrogen and copper–carbon monoxide, it was shown[2f] that by suitable procedures involving both equilibria and rates, activated adsorption and solution could be sharply differentiated, and the contributions of each to the total sorption under any conditions could be separately estimated. In the work here reported, the same methods have been applied in a study of the sorption of nitrogen, hydrogen and carbon monoxide by reduced iron.

No extensive investigations of sorption by iron have previously been reported. Sieverts[4] found the solubility of hydrogen in iron wire at 400° was very small, but increased with rising temperature; nitrogen dissolved in gamma but not in alpha iron. The "adsorptions" at lower temperatures have been examined by Taylor and Burns[5] and by Nikitin.[6]

Experimental Details

Since many of the experiments were continued over long periods, it was considered desirable to insure against leaks by substituting mercury seals for stopcocks. The apparatus has already been described.[2b] The sorption under any given conditions of pressure, temperature and time was determined as the difference between the volume of gas admitted to the bulb containing the iron, and the volume remaining in the free space. The latter was obtained by experiments with helium in the manner previously described.

The sorbent (Iron I, 54.6 g.) was prepared from an 8–14 mesh sample of fused ferroferric oxide, containing 0.15% of alumina, for which we are indebted to Dr. P. H. Emmett of the Fixed Nitrogen Research Laboratory, Washington. The oxide was reduced *in situ* in a current of hydrogen for five days at 375° and for fourteen days at 425–450°. Evacuation between runs was carried out at 500° by means of a Töpler pump.

Occasional check runs made at intervals throughout the work revealed no trend in the activity or capacity of the sample. Hence the data obtained for different gases, and for the same gas under different conditions, are directly comparable.

All volumes are given in cc. at 0°, 760 mm., and all pressures in mm. of mercury at 0°.

Results with Nitrogen

The isothermal adsorption of nitrogen at temperatures from −191.5 to 0° is shown in Fig. 1, Curves 1, 2, 3, 4. In this and later figures open circles indicate points obtained from lower pressures, that is, after a fresh addition of gas to the bulb; black circles (and other solid figures) are used for points obtained by the reverse process.

The rate of adsorption at −183, −78.5 and 0° was apparently instantaneous. At −191.5° equilibrium was attained in a few minutes. The fact that the equilibrium was actually reached is shown by the close agreement of points obtained from higher and from lower pressures.

[3] Benton and Elgin, THIS JOURNAL, **48**, 3027 (1926); **49**, 2426 (1927).

[4] Sieverts, *Z. physik. Chem.*, **60**, 129 (1907).

[5] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

[6] Nikitin, *J. Russ. Phys.-Chem. Soc.*, **58**, 1081 (1926); *Z. anorg. allgem. Chem.*, **154**, 130 (1926).

The observed effects of temperature and pressure, together with the practically instantaneous rates, leave no doubt that the sole process occurring here is a surface adsorption of the physical type. Thus, the isotherms show no tendency to reach a saturation limit, and at the higher temperatures the adsorption is very nearly proportional to the pressure.

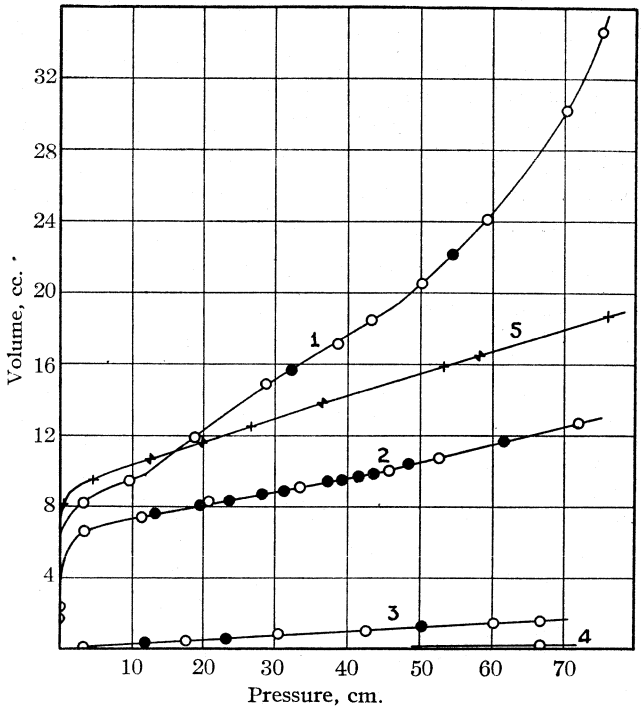


Fig. 1.—Isotherms for nitrogen and carbon monoxide: Curves 1, 2, 3 and 4 are for nitrogen at −191.5, −183, −78.5, and 0°, respectively. Curve 5 is for carbon monoxide at −183°.

Further, at a given pressure the values decrease uniformly with increasing temperature, and the heat of adsorption is relatively small, as shown by the values of Q, in cal. per mole, given in Table I.

TABLE I

HEAT OF PHYSICAL ADSORPTION OF NITROGEN BY IRON I

Vol. adsorbed	p at −191.5°	p at −183°	Q
8.0	22	190	3700
10.0	117	457	2340
12.0	195	641	2050

These heats cover the same range previously found for nitrogen on copper,[2f] and exceed the latent heat of vaporization of nitrogen (1380 cal.) by a factor of only 1.5 to 3.

Higher Temperatures.—The data obtained for the sorption of nitrogen at higher temperatures are given in Table II. These results were obtained by introducing a definite amount (5.91 cc.) of gas into the system, and successively determining the apparent equilibria at the temperatures shown.

TABLE II

SORPTION OF NITROGEN AT HIGHER TEMPERATURES

Temp., °C.	Pressure, mm.	Sorption, cc.
321	418.0	0.43
0	195.1	.42
344	425.1	.54
360	435.6	.56
408	469.6	.54
0	195.1	.42

The sorption at these higher temperatures is considerably greater than at 0°. Since here the physical adsorption must be negligibly small, it is evident that these values represent a second type of sorption. The rate of this process at 0° is very slow, so that little, if any, of the gas taken up at high temperatures is evolved on cooling to 0°.

The data obtained are incapable of furnishing a definite decision as to the nature of the high-temperature sorption. On the other hand, since Sieverts' experiments[4] indicate that gaseous nitrogen at ordinary pressures is insoluble in alpha iron, the evidence points to activated adsorption as responsible for the observed phenomena. This view is rendered still more probable by the fact that at the higher temperatures, iron similar to that here employed is known to activate nitrogen for ammonia synthesis,[7] and there is now available a large body of evidence to support the hypothesis that activated adsorption is an essential step in contact catalysis.

Results with Carbon Monoxide.—The isotherm for carbon monoxide at −183° is plotted in Fig. 1, Curve 5. Here as with nitrogen the rate was instantaneous. Throughout the whole range of pressure the ratio of the adsorption of carbon monoxide to that of nitrogen at this temperature is 1.44 ± 0.02. These facts are convincing evidence that in this case also the process is solely one of physical adsorption.

Measurements were also made with carbon monoxide at −78.5 and 0°, but in neither case was equilibrium reached, even after one hundred hours. Nevertheless, the observed rates clearly show the existence of two different processes. A few typical data on rates are given in Table III; the values shown for zero time are the volumes taken up at the last previous point.

At −78.5° a large fraction of the sorption occurred within three minutes (0.05 hour), after which the rate decreased sharply. At 0° relatively little sorption took place during the first three minutes, but after this time

[7] Almquist and Crittenden, *Ind. Eng. Chem.*, **18**, 1307 (1926).

TABLE III

RATE OF SORPTION OF CARBON MONOXIDE

−78.5°			0°		
Time, hrs.	P, mm.	V, cc.	Time, hrs.	P, mm.	V, cc.
0.0	0.0	0.95	0.0	2.0	1.66
.05	59.0	2.84	.05	191.4	2.40
12.1	29.0	4.00	.30	162.1	3.22
15.5	27.3	4.07	1.01	138.7	3.88
19.8	25.5	4.13	3.50	113.4	4.59
21.5	25.0	4.15	5.00	106.0	4.80
0.05	562.2	5.83	13.0	88.0	5.30
.80	555.2	6.10	35.6	70.0	5.82
14.7	530.3	7.07	74.8	57.7	6.16
27.4	521.8	7.40	0.05	503.7	6.48
38.6	515.9	7.63	1.22	490.7	6.84
50.7	511.4	7.80	5.9	469.8	7.43
62.9	508.9	7.90	21.8	438.0	8.32
87.2	503.4	8.11	50.2	413.2	9.02

the rate was more rapid than at the lower temperature, and the total sorptions reached after a given time were greater.

These results are precisely what would be expected if the total sorption at these temperatures is a combination of physical adsorption and a second process. Since other surfaces give *physical* adsorptions of carbon monoxide and nitrogen in this range of temperature, which are in the ratio[2f] of about 1.5, it may be calculated that here the adsorption of this type, at 500 mm. pressure, should amount to about 2 cc. at −78.5°, and about 0.2 cc. at 0°. Thus the first, rapid part of the observed sorption, which is much greater at −78.5° than at 0°, can be largely accounted for as physical adsorption. The nature of the subsequent process, whether activated adsorption, carbonyl formation or solution, or a combination of these, has not been ascertained.

Results with Hydrogen

Low Temperatures.—The adsorptions of hydrogen at −195 and −183° are plotted in Fig. 2, Curves 1 and 2. The striking discontinuities in these curves have previously been considered in detail, in connection with a general discussion of stepwise adsorption.[8] Neglecting the discontinuities, one observes that the general shape of the isotherms is typical of physical adsorption. There is little or no adsorption at "zero" pressure, and the values continue to increase with increasing pressure without approaching a saturation limit. At both temperatures the rate was apparently instantaneous, and values obtained from the side of higher pressure are in excellent agreement with those approached from lower pressures. The adsorptions decrease with rising temperature, and the heat of adsorp-

[8] Benton and White, THIS JOURNAL, **53**, 3301 (1931).

tion calculated from the isotherms by the Clapeyron equation is about 1600 cal. per mole. These observations show that physical adsorption is the sole process occurring.

Curve 3, Fig. 2, represents an isotherm at −78.5°. These results must be considered in the light of the following observations. The first two portions of gas admitted to the iron apparently came to equilibrium immediately at pressures of 50 and 258 mm., respectively, but the adsorption in each case was less than 0.05 cc. The next portion gave an immediate adsorption of 0.30 cc. at 715 mm. In each of these cases the pressure remained constant for the twenty to thirty minutes of observation. Part

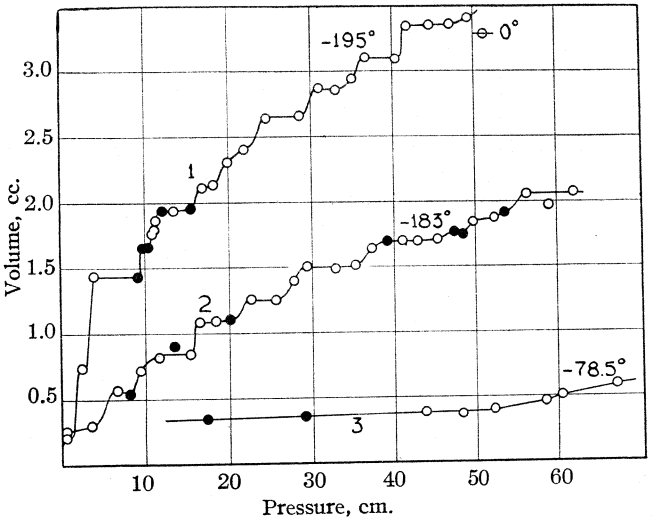


Fig. 2.—Isotherms for hydrogen.

of the gas was then withdrawn from the bulb, with the result that the adsorption at once decreased to 0.05 cc. at 405 mm. However, this volume did not remain constant, but gradually increased until an apparently constant adsorption of 0.28 cc. was reached after sixteen hours. From this point on, the values shown in Curve 3 were successively obtained. At each of these points equilibrium was established very rapidly; even with times of observation as long as twenty-two hours no change in adsorption occurred. A repetition of this experiment gave practically identical results, except that here the slow adsorption (0.24 cc. at 86 mm.) took place at the first point, where the system was kept under observation for thirty-nine hours.

The behavior noted is readily accounted for as follows. At −78.5° there is a small, rapid and readily reversible physical adsorption, which exhibits steps similar to those at lower temperatures, but here the first step

occurs at a pressure of about 600 mm. At one point in the course of following this isotherm, where sufficient time was allowed, a very slow activated adsorption of the order of 0.3 cc. occurred. The isotherm subsequently obtained represents the physical adsorption *plus* the 0.3 cc. adsorbed in the activated form. It is remarkable, however, that the activated adsorption, which reached 0.3 cc. in sixteen hours, showed no further increase in three days.

Higher Temperatures.—At 0° there was an immediate adsorption of 0.2–0.3 cc., followed by an extremely slow process which did not come to equilibrium in 35 days. The value reached at the end of this time, 3.28 cc. at 513 mm., is indicated in Fig. 2. At this point the temperature was quickly raised to 110°. The result was a rapid *decrease* of the sorption to 2.06 cc. at 768 mm., but this decrease was followed by a gradual *increase* over a period of three days to 2.47 cc. at 748 mm., without any sign of an approach to final equilibrium.

It may be concluded from these observations that in the neighborhood of 110° the sorption consists of two distinct processes, one of which is rapid and decreases in extent with increasing temperature, while the second is very slow. This conclusion is confirmed by isothermal measurements conducted wholly at 110°, which showed a rapid initial sorption followed

TABLE IV

RATE OF SORPTION OF HYDROGEN AT 110 AND 210°

Time, hrs.	110° P, mm.	V, cc.	Time, hrs.	210° P, mm.	V, cc.
0.0	...	0.0	0.0	...	0.0
.05	22.5	.23	.05	56.5	.38
.12	16.0	.35	.60	48.5	.51
.30	5.0	.58	2.7	45.0	.57
1.72	3.0	.62	6.1	43.0	.60
0.05	113.0	0.69	25.0	40.5	.64
.30	102.0	.92	0.05	539.3	1.02
.88	99.0	.98	2.0	522.1	1.30
1.63	97.0	1.02	5.0	516.1	1.40
4.38	93.9	1.08	21.0	505.9	1.57
8.13	92.0	1.12	30.5	503.0	1.62
21.7	88.0	1.20	45	500.5	1.66
0.1	315.0	1.42	54	499.6	1.67
1.0	310.0	1.53	69	496.8	1.72
3.0	307.1	1.59	78	496.1	1.73
7.3	303.4	1.66	96	493.7	1.77
24.7	297.7	1.78	117	492.4	1.79
0.05	607.7	1.91			
1.05	605.2	1.96			
4.6	602.2	2.02			
24.3	596.4	2.14			

by a very slow process. At 210° also there was a rapid process, which involved smaller quantities of gas than at 110°, and again a slow process ensued. The sorption at these temperatures as a function of time is given in Table IV.

At the conclusion of the measurements at 110°, when a sorption of 2.14 cc. had been reached, the system was rapidly cooled to −78.5°. At this temperature the sorption became constant almost immediately at 2.38 cc. under a pressure of 305.6 mm. It is evident that the gas taken up at 110° was not desorbed on cooling; on the contrary, an increase of about 0.2 cc. occurred, which is undoubtedly physical adsorption and is of the same order as the physical adsorption on the bare surface at −78.5°.

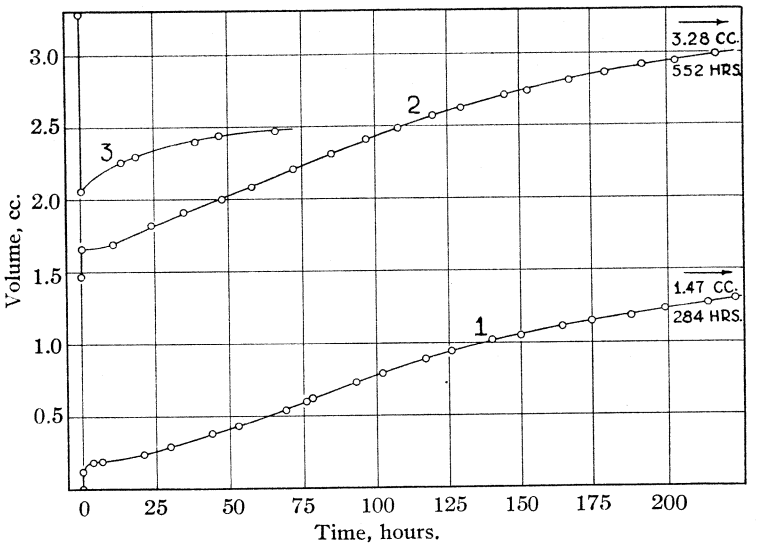


Fig. 3.—Rate of sorption of hydrogen at 0°: Curve 3, after heating to 110°.

The sorption at 0° as a function of time is shown in Fig. 3, Curves 1 and 2. The range of pressure involved here was as follows: for Curve 1, 120.5 to 72.7 mm; for Curve 2, 570.5 to 512.8 mm. In each case, after a rapid initial adsorption of about 0.2 cc., the rate sharply decreased almost to zero, then gradually increased, and finally fell off again. The change of sorption with time after heating to 110° is shown in Curve 3, which brings out clearly the rapid initial decrease of the sorption, followed by a slow increase.

In interpreting these results it is to be noted that the *physical* adsorption, which had already become very small at −78.5°, must be entirely negligible at 0° and above. The two processes which have been distinguished at 110° may provisionally be regarded as activated adsorption and solution.

On this basis the activated adsorption is very slow at 0°, except for the first 0.2–0.3 cc., but rapidly increases in rate with increasing temperature. The final equilibrium, on the other hand, corresponds to a decreasing activated adsorption with increasing temperature. If on a plot of the volumes taken up at 110 and 210° against the time, the slow process at these temperatures is extrapolated back to zero time, a rough estimate may be obtained of the fractions of the total sorption which are due to each individual process. In this manner it was found that (at 500 to 600 mm.) the activated adsorption amounted to about 1.4 cc. at 110° and 1.0 cc. at 210°; the slow process which has been ascribed to solution amounted to about 0.7 cc. at each temperature, but the time of observation was much longer at 210°, so that equilibrium was doubtless more closely approached. Because of the considerable uncertainty in these values, and because the slow process had certainly not reached equilibrium, the isobars for the different types of sorption will not be given here.

If the above view of the situation is correct, it must be concluded that the process of activated adsorption is *autocatalytic*. Thus at 0°, after about 0.2 cc. had been rapidly adsorbed, an induction period of eight to ten hours occurred, during which there was little further sorption. Subsequently the rate increased, passed through a maximum, and then decreased. This behavior is especially clearly shown by Curve 1 of Fig. 3. At 110°, in spite of the rapid rate of this process, there was some slight evidence of the same phenomenon. It is conceivable that only the few tenths of a cc. which was rapidly taken up at 0° (and slowly at −78.5°) represents activated adsorption, perhaps on the edges of the crystals, and that the autocatalytic process involves the formation of a new solid *phase* of iron hydride. Further data will be necessary before this possibility can be profitably discussed in detail. It may be noted, however, that on this view the rapid decrease in sorption on heating from 0 to 110° would indicate that the hydride is unstable at the latter temperature, even at a pressure of 770 mm.; consequently the rapid process at lower pressures observed in the experiments at 110 and 210° could not be ascribed to the formation of this definite hydride.

Discussion

The results for iron are similar in the main to those previously reported for nickel and copper. At low temperatures all three metals exhibit an apparently instantaneous physical adsorption, which decreases rapidly and uniformly with increasing temperature, corresponding to heats of adsorption which are only about two to four times the latent heat of vaporization of the several gases.

At some point activated adsorption first makes its appearance, and rapidly increases in rate at higher temperatures. On both copper and

iron the rate of this process is considerably greater for carbon monoxide than for hydrogen, and enormously greater than for nitrogen. Comparison of the different metals shows that the rates of activated adsorption of hydrogen were about equal for the particular samples of nickel and copper employed, but were much less in the case of iron. The rate with carbon monoxide was much less for iron than for copper. (The system nickel–carbon monoxide has not been studied from this point of view.) Doubtless the smaller rates with iron are due in part to the fact that the sample of iron was prepared from fused oxide by reduction at a high temperature, while the other two metals were obtained by cautious ignition of their nitrates and reduction at much lower temperatures.

In many of the cases studied, a third process, provisionally ascribed to solution, has been definitely distinguished. Such a process occurs in the system, iron–hydrogen. With nitrogen and carbon monoxide in contact with iron, this third process is not apparent, but it must be noted that in these latter cases the sorptions have been less extensively examined.

Multimolecular Layers at Low Temperatures.—Inspection of Curves 1 and 2 of Fig. 1 reveals the fact that definite "breaks" occur in each case at an adsorption of about 10 cc. This is apparently the volume of nitrogen necessary to form a complete unimolecular layer of molecules over the surface. The sharpness of the breaks is no doubt diminished by the incipient formation of a second layer before the first is entirely completed. At $-191.5°$ there is a second, less definite break at a volume of 19–20 cc., which presumably signifies the completion of the second layer of molecules. From this point on, the adsorption appears to increase in a regular manner, gradually approaching infinity as the pressure increases toward the vapor pressure of liquid nitrogen at this temperature (about 110 cm.).

On this basis the physical adsorptions at the higher temperatures correspond to a very incomplete covering of the surface with a single layer of molecules. It may be of interest to point out also that the activated adsorption of the various gases never amounts to as much as 10 cc. From this fact the conclusion may be drawn that activated adsorption does not exceed a unimolecular layer, although the latter is closely approached in the case of carbon monoxide at 0°.

Summary

The isothermal sorptions of nitrogen, carbon monoxide and hydrogen by reduced iron have been measured at pressures up to one atmosphere and over a range of temperatures down to 78°K. In many cases also the change in sorption with change in temperature has been examined, with a constant volume of gas in the system.

As in the case of copper previously reported, it is found that in general sorption involves three definitely distinguishable processes, (a) *ad*sorption

of the physical type, (b) *ad*sorption of the activated type and (c) a third process which is probably solution. The contribution of the individual processes to the total observed sorption has been estimated.

The distinguishing characteristics of each process have been further elucidated, particularly in respect to rates, equilibria, heats and thickness of adsorbed layers.

With all three gases at −183° and below, the sorption consists solely of physical adsorption. In each case activated adsorption occurs at higher temperatures. The rate of this process is greatest for carbon monoxide and least for nitrogen. With hydrogen at 110° and above, the third process, ascribed to solution, comes into prominence.

UNIVERSITY, VIRGINIA

[CONTRIBUTION NO. 88 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.]

THE REACTION BETWEEN OXYGEN AND PROPYLENE: ACTIVATION, OXIDATION AND POLYMERIZATION

BY SAMUEL LENHER

RECEIVED DECEMBER 14, 1931 PUBLISHED MAY 7, 1932

It was recently shown in a study of the reaction between oxygen and ethylene[1] that activation of ethylene was a primary process in the reaction. This activation led to the formation of polymerization and pyrolysis products from ethylene, as well as oxidation products, under conditions where pure ethylene is not decomposed. The formation of the primary oxidation products, ethylene oxide and acetaldehyde containing one oxygen atom and the elements of ethylene in the molecule, and the formation of the polymerization products, propylene, butylenes and amylenes, without separation of hydrogen or direct formation of saturated hydrocarbons or carbon, showed that the activation of ethylene consisted in an activation of the double bond. Since the primary oxidation and decomposition reactions of ethylene could be interpreted adequately by assuming an activation of the double bond under the influence of heat or of oxygen, it seemed of value to determine whether the next member of the monoolefin series of hydrocarbons, propylene, behaved similarly. The work described in this paper leads to the conclusion that activation of the double bond in propylene is the primary process in the oxidation and polymerization reactions.

The oxidation of propylene has received little attention. In connection with the study of the oxidation of ethylene[2] some experiments on the oxidation of propylene at 280–315° showed that the liquid products of the

[1] Lenher, THIS JOURNAL, **53**, 2420, 3737, 3752 (1931).

[2] Lenher, Ref. 1, p. 3748.

reaction were propylene oxide, propionaldehyde, acetic acid, acetaldehyde, formic acid, formaldehyde and a peroxide compound, and that the mechanism of the slow oxidation was very similar to the oxidation of ethylene.

The thermal decomposition of propylene has recently been the subject of several investigations. However, a survey of these researches gives no clear picture of the principal primary reactions involved in the pyrolysis of propylene. Frey and Smith[3] concluded from a study of the decomposition of propylene at 575° and 760 mm. in a silica vessel with a time of contact of five minutes that the principal products of the polymerization of propylene (under these conditions) were butylene and higher hydrocarbons, as well as large amounts of methane and ethane. Their results show that the principal products were methane 10.4% ethylene 8.0%, propane 3.0%, butylene 2.8%, C_nH_{2n}(n = 5 to 8) 2.6% ethane 1.9% and hydrogen 1.7%. Wheeler and Wood[4] studied the decomposition of propylene at 650° in silica vessels at times of contact of twenty seconds and longer and reported the principal products to be ethylene, ethane, and butylene with small amounts of aromatic hydrocarbons. Recently Hurd and Meinert[5] reported on the pyrolysis of propylene in Pyrex glass and quartz at temperatures between 600 and 950° and times of contact of from half a second at 950° to thirty seconds and up to two minutes at the lower temperatures. They found that under their conditions propylene broke down to form simpler gases, the principal products being methane, ethylene, hydrogen, and paraffins higher than methane (principally ethane) in the ratio 3:3:1:1. The mechanism of the pyrolysis of propylene was considered to be the same as that suggested by Hurd and Spence[6] to explain the pyrolysis of isobutylene involving breaking of C—C and C—H bonds and a possible activation of the C=C bonds. Dunstan, Hague and Wheeler,[7] in a survey of the pyrolysis of the lower olefins, concluded that the principal primary reaction, common to all, was the formation of either two-carbon or four-carbon atom (or both) members of the mono-olefin series. They considered that the primary reaction in the pyrolysis of propylene was $2C_3H_6 = C_2H_4 + C_4H_8$.

Experimental

The reaction between propylene and oxygen, and the pyrolysis of oxygen-free propylene, were studied in the recirculation apparatus described in detail in a previous communication[8] using the same experimental procedure. A preheater and reaction vessel of fused silica were used in all the experiments. The only change in the apparatus was the use of a smaller charcoal absorption tube 24 mm. by 30 cm. containing 100 g. of

[3] Frey and Smith, *Ind. Eng. Chem.*, **20**, 950 (1928).
[4] Wheeler and Wood, *J. Chem. Soc.*, 1823 (1930).
[5] Hurd and Meinert, THIS JOURNAL, **52**, 4978 (1930).
[6] Hurd and Spence, *ibid.*, **51**, 3561 (1929).
[7] Dunstan, Hague and Wheeler, *J. Soc. Chem. Ind.*, **50**, 316T (1931).
[8] Lenher, Ref. 1, p. 3752.

charcoal, for the recovery of the higher olefins formed. The small amount of charcoal was used because the large volume of propylene absorbed by the charcoal made use of a larger amount impracticable to handle in a recovery system. The oxidation products were determined as outlined in the previous papers on ethylene oxidation.[9] Propylene was taken from commercial cylinders (Carbide and Carbon Chemicals Corporation). Fractional distillation showed it to be free from other olefins. Analysis showed the gas to be 98.0% propylene, 1.5% propane, 0.13% carbon dioxide and the remainder inerts, probably nitrogen.

Gas analyses were carried out in a Burrell gas analysis apparatus (Precision Type). The procedure of Hurd and Spence,[10] based on the differential absorption of the lower olefins in sulfuric acid of various concentrations, was used for the analysis of the unsaturated hydrocarbons (acetylene hydrocarbons absent). The directions given by Hurd and Spence were checked and found to be entirely satisfactory and dependable for the analysis of a mixture of ethylene, propylene and butylenes, or a complex mixture of these gases with carbon oxides, hydrogen and lower saturated hydrocarbons.

The higher olefins formed in the reaction and absorbed on the charcoal were recovered as liquids by heating the charcoal to 130–140° in a flask and steaming thoroughly. The gases and steam evolved were cooled with a long condenser and a water scrubber. The hydrocarbon products were recovered in a long spiral trap which was cooled in boiling liquid ammonia following the scrubber. As propylene boils at −47° and the temperature of boiling liquid ammonia is −38.5° the excess of propylene from the absorbent charcoal was not condensed with the products. The identity of the hydrocarbon products was established by fractional distillation, giving the boiling point of each constituent, and by chemical tests and analyses. The hydrocarbons boiling below propylene, which were not absorbed by the charcoal saturated with propylene, were allowed to build up together with carbon oxides in the recirculation system, and were determined by gas analysis at the end of a run. The amount of propylene consumed in a run, as calculated from the composition of the oxidation and pyrolysis products, agreed within 10% with the propylene consumption indicated from the observed volume change in the system and the initial and final composition of the gas.

The results of a number of experiments carried out with the recirculation apparatus are summarized in Table I and Table II. The runs were all carried out with high propylene and low oxygen concentrations; the gas at the start of a run was 90% propylene, the remainder being air and carbon dioxide. Oxygen was supplied to the system during the run at approximately its rate of consumption. The average duration of the experiments was four hours.

The experiments in Table I show that under the conditions outlined at temperatures between 500–600° and times of contact of less than eight seconds the oxidation products of propylene are simple in nature. The only oxidation products resulting in amounts sufficient for analysis were acetaldehyde and formaldehyde (grouped as total aldehyde in Table I), formic acid, carbon oxides and water. No evidence was obtained of the presence of propylene oxide or of propionaldehyde which are formed in the oxidation of propylene at lower temperatures.[11] It is probable that

[9] Lenher, Ref. 1, pp. 3744, 3753.

[10] Ref. 6, p. 3356.

[11] Lenher, Ref. 1, p. 3748.

TABLE I

REACTION BETWEEN PROPYLENE AND OXYGEN IN RECIRCULATION APPARATUS USING PACKED PREHEATER AND ONE LITER REACTION VESSEL OF FUSED SILICA

Expt.	Temperature, °C. Reaction vessel	Pre-heater	Time of contact, sec.	Initial composition of gas, % C_3H_6	O_2	Propylene consumed, g.	Yield of products in % of propylene consumed: Oxidation products	Higher olefins	Saturated hydrocarbons
1	518	490	3.7	87.5	0.5 to 1.0 cc./sec. fed in during run	1.88	73.2[a]	26.8	..
2	516	510	7.8	83.8		7.61	38.3[b]	61.6	..
3	500	530	7.8	90.9		7.74	48.0[c]	52.0	..
4	600	585	6.9	91.2		20.61	18.7[d]	52.6	28.6
5	510	502	7.8	91.9	No O_2	0.0	0.0	0.0	0.0
6	590	570	7.0	92.1	No O_2	2.76	0.0	68.1	31.9

[a] Total aldehyde 35.1%; HCOOH 2.0%; CO_2 36.1%

[b] Total aldehyde 16.1%; HCOOH 1.2%; CO_2 21.0%

[c] Total aldehyde 30.1%; HCOOH 1.1%; CO_2 16.8%

[d] Total aldehyde 10.6%; HCOOH 0.3%; CO_2 5.0%; $CO + H_2$ 2.8%

TABLE II

COMPOSITION OF OLEFIN PRODUCTS OF REACTION OF PROPYLENE WITH OXYGEN

Expt.	Composition of olefin products, % of propylene reacted C_4H_8	C_5H_{10}	C_6H_{12}	Higher members
1	26.8	..	..	..
2	28.5	14.8	55.9	..
3	23.4	23.0	53.6	..
4	9.3	27.4	32.3	30.4[a]
6	17.8	13.2	68.2	..

[a] 11.3 boils 70–85°; 19.1 boils above 85°.

they were formed and were rapidly oxidized and decomposed at the high temperatures of the present experiments.

Experiments 1 to 3 show that in addition to oxidation, pyrolysis of propylene takes place, yielding hydrocarbon products. The only hydrocarbons resulting from this decomposition of propylene at temperatures below 530° are higher olefins, butylenes, amylenes and hexylenes. Experiment 5 with pure, oxygen-free, propylene shows that it is unchanged at 510° and times of contact of eight seconds in a silica vessel. A comparison of Expts. 1 to 3 with Expt. 5 shows that pyrolysis of propylene is effected by oxygen under conditions where pure propylene is thermally stable. This activated pyrolysis of propylene is such an important reaction that with small amounts of oxygen (Expts. 2 and 3) more propylene is pyrolyzed or polymerized, than is oxidized. It is noteworthy that in this activated pyrolysis resulting in the formation of higher olefins there was no formation of oil or tar observed below 600°. At higher temperatures of around

600° saturated hydrocarbons are formed both in the pyrolysis of propylene activated by oxygen (Expt. 4) and in the pyrolysis of oxygen-free propylene (Expt. 6). With pure propylene at 590° over two-thirds of the products of pyrolysis are olefins and one-third is saturated hydrocarbons with two carbon atoms in the molecules and with propylene activated by oxygen at 600° of the hydrocarbon products 64.8% is higher olefins, and 35.2% is saturated hydrocarbons with two carbon atoms in the molecule. As higher mono-olefins are the only hydrocarbon products of the pyrolysis of propylene activated by oxygen at 500°, it can be concluded that higher mono-olefins are the primary products of the pyrolysis of propylene and that the saturated hydrocarbons formed at higher temperatures are the result of secondary decompositions of the primary products.

The higher olefin reaction products were dried over solid potassium hydroxide and distilled from fresh potassium hydroxide. They were water-white limpid liquids of density less than 1. They had the characteristic olefinic odor, they absorbed bromine forming liquid bromides, decolorized permanganate solution rapidly in the cold, and were insoluble in water. The dried mixture of hydrocarbons was fractionated in a small still. The fraction boiling from −6 to 0° was assumed to be butylene, after the above chemical tests. In Expts. 1, 2 and 3 sharp fractions at −6° to 0°, 30–38° and 60–65° were the only products. The fraction boiling from 30–38°, where the amylenes boil, was assumed to be amylenes. On microcombustion the composition of this fraction was found to be C = 87.25%, H = 12.71%; theoretical for C_nH_{2n} is C = 85.7%, H = 14.3%. The fraction boiling from 60–65°, where the hexylenes boil, was assumed to be hexylenes. This fraction on microcombustion showed its composition to be: C = 86.71%, H = 12.41%. In Expt. 4 at 600° the dried hydrocarbon products recovered from the absorbent charcoal, after distilling off butylenes (−6 to 0°) boiled over the range 30 to 85° with two main fractions at 30–40° and 60–69°. The 30–40° fraction analyzed C = 87.85%, H = 11.27%, and the 60–69° fraction analyzed C = 87.90%, H = 11.41% by microcombustion. Redistillation of these fractions from solid potassium hydroxide and storing over anhydrous magnesium sulfate did not change the analysis. The boiling ranges of the various fractions together with their physical and chemical properties show that they were olefin hydrocarbons. The fractions probably contained small amounts of dienes, as 1,3-pentadiene b. p. 42°, 2,3-pentadiene b. p. 49–51°, and 1,3-hexadiene b. p. 72–74°, which would change the ratio for carbon to hydrogen from the theoretical for C_nH_{2n} in the direction of the higher carbon and lower hydrogen percentages found by analysis. There was no evidence of the formation of detectable amounts of cycloparaffins.

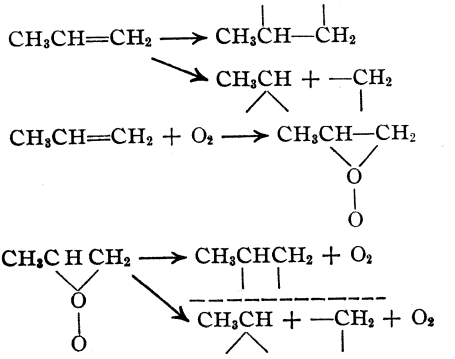
A check on the entire experimental procedure was made by filling the system with propylene, saturating the charcoal and circulating the gas

with the reaction vessel at room temperature. The charcoal was then removed and heated to 140° and steamed. No liquid hydrocarbons, other than propylene, were separated in the recovery system. It is clear that the hydrocarbons recovered after an experiment had been formed in the reaction and had not come from the original propylene as contamination or been formed from propylene in the absorbent charcoal on recovery.

Discussion

These experiments show that propylene containing small amounts of oxygen undergoes a polymerization reaction as well as oxidation and that the primary products of this polymerization are higher mono-olefins. The data show further that oxygen activates this pyrolysis of propylene to take place more rapidly at a lower temperature than is the case in its absence.

Since the pyrolysis of propylene activated by oxygen takes place in its initial stages without separation of carbon or hydrogen or formation of saturated hydrocarbons, the occurrence of mono-olefin products must be due to an activation of the hydrocarbon which will allow it to react with itself without changing the ratio of carbon to hydrogen. This activation consists in an opening up of the double bond by heat, or oxygen. It has been shown in the similar behavior of ethylene that this activation may lead to the formation of activated hydrocarbon molecules by the breaking of one of the carbon double bonds, and to the separation of methylene radicals by a scission of the two carbon double bonds; these considerations[12] may be taken to apply without modification to the oxidation, activation and polymerization of propylene. The first step in the reaction is an activation of the double bond by heat or oxygen



Butylene is formed by a reaction of a methylene radical with propylene



[12] Lenher, Ref. 1, p. 3756.

The amylenes may be formed in a reaction between an ethylidene residue and propylene

$$\begin{array}{l} CH_3CH \\ \diagup\!\diagdown \end{array} + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CH{=}CH_2 \qquad (4)$$

As both butylenes and amylenes occur in amounts which are smaller than the amount of hexylene, the formation of hexylene is the most important reaction. Hexylene is formed in the reaction of an activated propylene molecule with a normal propylene molecule, as

$$\begin{array}{l} CH_3CH{-}CH_2 \\ \quad|\quad| \end{array} + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CH_2CH{=}CH_2 \qquad (5)$$

This reaction presents certain theoretical difficulties as it is a bimolecular association reaction, but it appears from a recent speculation of Kassel[13] that such reactions are possible.

This outline of the activation and pyrolysis of propylene explains satisfactorily the observed products and the probable mechanism of the primary processes involved. Recent investigators of the pyrolysis of propylene[3,4,5] have concluded that the principal primary products are other than those obtained in the present work. These results of other investigators are not actually in conflict with the present findings; they show that these authors were not dealing with the primary products of the pyrolysis of propylene but that the products which they obtained were the result of a more profound decomposition which carried the pyrolysis beyond the primary stage. The present experiments carried out at low temperatures and short times of contact have enabled the isolation of the primary products to be made. Wheeler and Wood's own work[4] on the pyrolysis of the butylenes shows that when they break down at 600° at longer times of contact than were used in this paper, they yield propylene, ethylene, ethane, methane and hydrogen, and it may be assumed that the C_5 and C_6 olefins yield similar simple products under the same conditions. This pyrolysis of higher mono-olefins formed as the primary products on heating a longer time accounts for the simpler olefin and paraffin hydrocarbon products obtained by Frey and Smith, Wood and Wheeler and Hurd and Meinert. It is evident, therefore, that the primary products of the pyrolysis of propylene are higher mono-olefins and that ethylene, simple paraffins and hydrogen result from secondary reactions. The formation of aromatics occurs only above the temperature range considered in this paper.

The similarity between the behavior of ethylene and of propylene in their oxidation and pyrolysis reactions shows that the mechansim of these reactions which has been outlined above and in a previous paper[12] is general for the mono-olefin series of hydrocarbons.

[13] Kassel, THIS JOURNAL, **53**, 2143 (1931).

Summary

The reaction between propylene and oxygen at high propylene and low oxygen concentrations has been studied in a recirculation apparatus between 500 and 600°. In addition to oxidation of propylene, pyrolysis of propylene takes place.

The oxidation products were acetaldehyde, formaldehyde, formic acid, carbon oxides and water.

The primary products of the pyrolysis were higher mono-olefins, butylenes, amylenes and hexylenes. Secondary products of pyrolysis are olefins, paraffins and hydrogen.

The temperature at which pyrolysis of pyropylene is appreciable is lowered greatly by the presence of small amounts of oxygen, and the rate of pyrolysis is markedly increased.

A mechanism of the oxidation and pyrolysis of propylene based on the activation of the carbon double bond has been outlined.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 307]

THE GAS PHASE EQUILIBRIUM BETWEEN METHYL NITRITE, HYDROGEN CHLORIDE, METHYL ALCOHOL, AND NITROSYL CHLORIDE. THE ABSORPTION SPECTRUM OF NITROSYL CHLORIDE

BY J. A. LEERMAKERS AND H. C. RAMSPERGER

RECEIVED DECEMBER 16, 1931 PUBLISHED MAY 7, 1932

Free energy values of organic substances will probably most often be obtained from heats of combustion and specific heat data by use of the third law of thermodynamics. They may, of course, be obtained with considerable accuracy from equilibrium data, but often a good equilibrium free from side reactions cannot be obtained with organic compounds. It is still more unusual to establish a gas phase equilibrium at room temperature. In the course of an investigation by the junior author to locate a gas phase reaction suitable for reaction rate research it was found that an equilibrium was very rapidly established between the gases listed in the title at room temperature. This was shown by the immediate partial disappearance of the color of nitrosyl chloride gas when added to an excess of methyl alcohol gas, and the appearance of the same color when hydrogen chloride gas was added to methyl nitrite gas. The thermodynamic data for the three gases, methyl alcohol, nitrosyl chloride and hydrogen chloride are quite accurately known so that from equilibrium measurements at two temperatures we are able to calculate the free energy of formation, the heat of formation and entropy of methyl nitrite.

Experimental Method

The equilibrium concentrations were obtained by quantitative measurements of the absorption of light in the spectral region 4000 to 5000 Å., where the absorption of nitrosyl chloride is quite strong. Of the other substances only methyl nitrite absorbs light in this region and then only faintly between 4000 and 4200 Å. From our determination of the absorption of pure nitrosyl chloride and methyl nitrite, the absorption of an equilibrium mixture of the four substances and the initial pressures of two of them it is possible to calculate an equilibrium constant for the reaction

$$CH_3ONO\ (g) + HCl\ (g) = CH_3OH\ (g) + NOCl\ (g)$$

Preparation and Purification of the Compounds.—Nitrosyl chloride was prepared by passing hydrogen chloride into nitrosyl sulfuric acid obtained from sulfur dioxide and fuming nitric acid.[1] The nitrosyl chloride was repeatedly distilled and collected at $-20°$ to remove traces of hydrogen chloride and finally fractionally distilled through a column surrounded by a bath at $-25°$. The middle fraction boiling at $-6.0 \pm 0.2°$ was used. This was distilled at a low temperature on a high vacuum line into a number of small tubes each drawn down to a capillary and maintained at $-78°$. When sufficient nitrosyl chloride had collected in a small tube, the supply was also cooled to $-78°$ stopping the distillation and the tube was sealed off.

Methyl nitrite was prepared by dropping sulfuric acid into a stirred and gently heated mixture of sodium nitrite and methyl alcohol. The evolved gas was passed through fused calcium chloride and collected at $-78°$. The liquid was fractionally distilled through a column surrounded by ether cooled by solid carbon dioxide to about $-30°$ and was collected at $-78°$. It boiled at a constant temperature of $-17.0°$ and the middle portion was used. It was found necessary to eliminate traces of nitrogen dioxide since the strong characteristic absorption bands of this substance interfered with the measurements. A supply of pure methyl nitrite was obtained by allowing the gas to pass through a long tube containing soda lime into a one-liter storage flask sealed onto the vacuum system and previously evacuated. No bands of nitrogen dioxide were then found in the sample even when a pressure of the gas as high as 40 cm. was in the absorption tube.

The methyl alcohol used was Baker's Analyzed absolute methyl alcohol. This was further dried by refluxing over aluminum amalgam and was then fractionally distilled. It was placed in a small receiver equipped with a stopcock, sealed to the vacuum system, and enough of the vapor pumped off to displace all of the air.

Hydrogen chloride was obtained by dropping C. P. hydrochloric acid on concentrated C. P. sulfuric acid. The hydrogen chloride gas was passed through wash bottles containing concentrated C. P. sulfuric acid, then through a tube filled with C. P. anhydrous calcium chloride, and was collected in a half-liter flask equipped with a stopcock and a tube sealed to the bottom. When gas sufficient to displace the air had passed through the flask the stopcock was closed and the entrance tube sealed off. The flask was sealed to the vacuum system and the hydrogen chloride was frozen down by means of liquid air into the tube at the bottom. Any air left in the flask was then pumped off, the stopcock was closed, and the solid hydrogen chloride allowed to evaporate into the flask. It was used without further treatment.

The Absorption Curve of Nitrosyl Chloride and Methyl Nitrite.—A Pyrex absorption cell 4 cm. in diameter and 40.0 cm. long with plane parallel windows was filled with ni-

[1] Scott and Johnson, *J. Phys. Chem.*, **33**, 1975 (1929).

trosyl chloride or methyl nitrite gas as shown in Fig. 1. The absorption cell A was evacuated with a mercury diffusion pump through G. It was filled with nitrosyl chloride by breaking the capillary end of the tube B containing liquid nitrosyl chloride with the magnetic hammer C, or filled with methyl nitrite from the supply D.

The pressure was measured by a "clicker" system. The pressure on the "clicker"[2] sealed in the bottom of the bulb F was controlled by the variable leaks J or by vacuum through H and was measured by a McLeod gage having a compression of about eight-fold so as to read accurately pressures of several cm.

The absorption cell was then immediately sealed off just above the side tube. Capillary tubing was used to prevent too much reaction of nitrosyl chloride with the grease of the stopcock before sealing off.

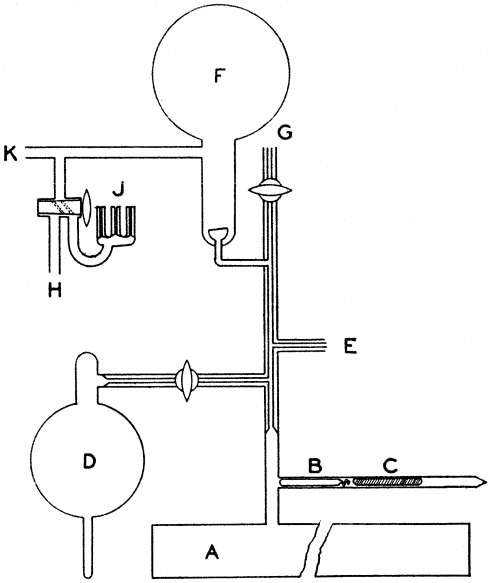


Fig. 1.

Figure 2 shows the apparatus for photographing the absorption spectrum. Light from the 40-watt mazda lamp B operating under constant voltage passes through the diaphragm C which is covered with a ground glass, then through the partition D, the shutter E, the diaphragm F, the absorption cell H containing the absorbing substance, the diaphragm F′, and finally into the slit of the spectrograph N. The cell is attached to the galvanized iron thermostat by the large rubber tubes at G and G′ which slip over the brass tubes soldered into the ends of the thermostat. The cell has a side tube J (not shown in Fig. 1) used for freezing out the contents of the cell with liquid air. K is a heater and stirrer, L the mercury thermo-regulator and M is a thermometer which was calibrated against a Bureau of Standards thermometer.

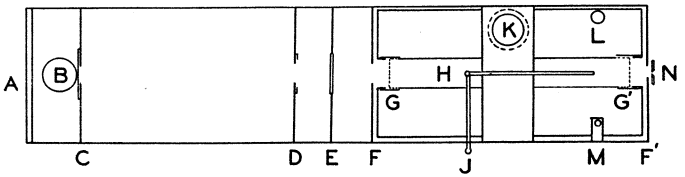


Fig. 2.

A series of spectra are photographed with the absorbing medium in the cell, the cell contents are frozen out, and then a series of photographs are taken on the same plate in between the first exposures. These latter exposures are given the same exposure time but are uniformly reduced in intensity for all wave lengths by placing screens of known absorption in the light path at D. The blackening of the photographic plate on two adjacent spectra is the same for those wave lengths for which the particular screen and the gas in the cell have the same absorption. Positions of equal intensity were deter-

[2] Smith and Taylor, THIS JOURNAL, **46**, 1393 (1924).

mined by a method similar to that used by Ramsperger and Porter.[3] The photometer system for this purpose is shown in Fig. 3. The photographic lens D projects an image of the plate in the holder C on the screen L with a magnification of about eight times. A high light intensity is obtained by the 500-watt projection lamp A and the condensing lenses B. A slit in the screen 2 cm. long and 2 mm. wide allows the light from a very narrow region of the spectrum to fall onto a cesium photoelectric cell E. F is a 45-volt battery, G a 10-megohm resistance, H a Leeds and Northrup high-sensitivity galvanometer with critical damping resistance J. With a scale at two meters, deflections of 6 to 20 cm. were obtained. The plate in the holder C could be moved either vertically or horizontally so as to bring the image of the spectra on the slit at any wave length. Points of equal deflection could be located with an accuracy of 2 to 5 Å. An iron arc spectrum served as a wave length reference. We wish to thank Professors Dickinson and Beckman of this Laboratory for the use of the screens which were constructed and calibrated by them. They determined the transmission of the screens by use of a thermopile and a constant light source.

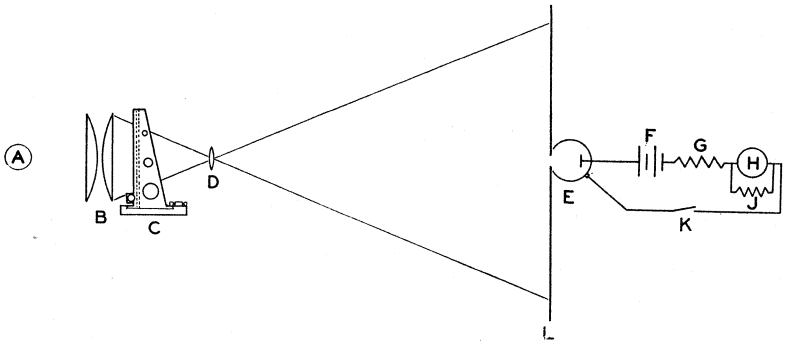


Fig. 3.

Table I gives the data obtained for the absorption of nitrosyl chloride and methyl nitrite at temperatures of 25 and 50°. The pressures are calculated to 25°. The absorption coefficients at the wave lengths listed are then calculated by assuming that Beer's law is obeyed over the range of pressure investigated. The relation used was $I_t/I_0 = 10^{-\epsilon cd}$ where I_t/I_0 is the fraction of light transmitted, c is the concentration expressed in cm. of mercury pressure at 25°, d is the length of the absorption cell (40.0 cm.) and ϵ is the absorption coefficient. Values of ϵ are plotted against the wave length in Fig. 4.

The small circles on the dotted line portion of the curve at 25° were estimated from the difference in galvanometer deflections from the nearest points of equal intensity on one of the plates. This region of the curve was not used in determinations of the equilibrium concentrations of nitrosyl chloride. The coincidence of several points at different pressures indicates that Beer's law is obeyed fairly well in the range studied.

The Partial Pressure of Nitrosyl Chloride at Equilibrium.—When nitrosyl chloride of concentration c and of absorption coefficient ϵ_1 is present

[3] Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926).

TABLE I

POINTS OF EQUAL INTENSITIES (ÅNGSTRÖM UNITS) ON PHOTOGRAPHS TAKEN THROUGH SCREENS AND THROUGH NITROSYL CHLORIDE AND METHYL NITRITE AT VARIOUS TEMPERATURES AND PRESSURES

Screen no.	Light transmitted by screen	NOCl 3.86 cm. 25°	NOCl 3.86 cm. 50°	NOCl 11.02 cm. 25°	NOCl 11.02 cm. 50°	NOCl 8.44 cm. 25°	NOCl 8.44 cm. 50°	CH_2ONO 41.84 cm. 25°	CH_2ONO 41.84 cm. 50°
2	0.459	4960	4940					4108	4115
		4530	4543						
		4520							
3	.2395	4170	4190					4065	4080
		4168[a]							
4	.1032	4005	4010	4960	4945	4862	4855	4037	4045
		4007[a]		4550		4255	4642		
				4505		4653	4432		
5	.0553			4850	4847	4186	4208	4018	4025
				4650	4647				
				4263	4406				
					4340				
					4295				

[a] Duplicate plate to check accuracy.

in the same cell with methyl nitrite of concentration c_2 and absorption coefficient ϵ_2 the Beer's law expression becomes $I_t/I_0 = 10^{-(\epsilon_1 c_1 + \epsilon_2 c_2)d}$. If

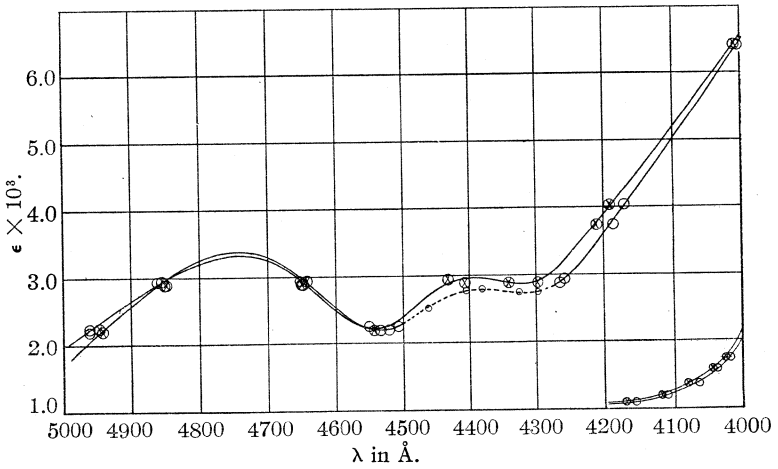


Fig. 4.—Absorption coefficients of nitrosyl chloride and of methyl nitrite plotted against wave lengths. The two upper curves are for nitrosyl chloride; those in the lower right-hand corner are for methyl nitrite. The open circles are for 25°, the circles enclosing crosses are for 50°.

the initial concentration of nitrosyl chloride is a and its equilibrium concentration after adding methyl alcohol is x, the expression becomes $I_t/I_0 = 10^{-\{\epsilon_1 x + \epsilon_2(a-x)\}d}$.

The same expression results if, in starting with methyl nitrite and hydro-

gen chloride, a is the initial concentration of methyl nitrite. The equilibrium concentration x can then be calculated from values of ϵ_1 and ϵ_2 obtained from the absorption curve for the wave length at which I_t/I_0 is measured.

The cell was filled with the two initial substances and their pressures were determined as described before and shown in Fig. 1. Methyl alcohol or hydrogen chloride was attached at E. Capillary tubing was used as indicated so that when the cell was sealed off just above the side tube no appreciable error was made in the partial pressures of gases admitted even though perfect mixing in the tubing had not taken place. The procedure in making the exposures and finding the points of equal intensity was similar to that for determining the absorption curves for the pure gases. Table II gives the complete data of two experiments. Table III gives a summary of all of the experiments.

TABLE II

SAMPLE EXPERIMENTS

Exposure	Absorbing medium	Points of equal intensity, Å.	Pressure NOCl
	Expt. 4b. CH_3ONO, 4.03 cm.; HCl, 7.45 cm.; T, 50°		
1	Cell and contents	4235	2.43
2	Screen No. 2	4230	2.39
3	Cell and contents		
4	Iron arc source		
5	Cell and contents	4043	2.47
6	Screen No. 3	4037	2.44
7	Cell and contents		
			Average 2.43
	Expt. 5a. CH_3ONO, 5.90 cm.; HCl, 3.07 cm.; T, 25°		
1	Cell and contents		
2	Screen No. 2	4125	1.69
3	Cell and contents	4123	1.69
4	Iron arc source		
5	Cell and contents		
6	Screen No. 3	4000	1.72
7	Cell and contents	4003	1.73
			Average 1.71

TABLE III

SUMMARY OF EXPERIMENTS

Expt. no.	Initial pressures, cm. CH_3ONO	HCl	NOCl	CH_3OH	Pressure of NOCl at equilibrium 25°	50°	K_{298}	K_{323}
4	4.03	7.45			2.26 ± 0.04	2.43 ± 0.02	0.556	0.735
5	5.90	3.07			1.71 ± .01	1.88 ± .02	.513	.739
6			4.58	2.87	2.47 ± .02		.422	
7			4.56	4.14	2.04 ± .03	2.26 ± .03	.520	.785
8			12.70	3.44	9.64 ± .10	9.78 ± .09	.391	.596
12			6.02	4.06		3.44 ± .10		.764
13			4.75	4.19	2.14 ± .01	2.26 ± .06	.497	.620
14			4.20	3.76		2.07 ± .03		.744

Experiments 1 and 2 are not included because they were preliminary experiments made before the apparatus was in its final form. In Expts. 3, 9, 10 and 11 the total pressure in the cell was sufficiently high so that there was some evidence of condensation in each case. The equilibrium pressures of nitrosyl chloride are generally the average of four points. The average deviation from the average is shown by the ± sign in columns 6 and 7. Equilibrium constants have been calculated by assuming the fugacities of the gases equal to their pressures. Experiments 6 and 8 deviate rather badly from the others listed. In these cases the concentration of methyl alcohol at equilibrium is very low, in fact so low that the estimated experimental error in the measurement of the nitrosyl chloride pressure will produce a very large error in the equilibrium constant. These experiments have not been used in obtaining an average equilibrium constant. Experiment 13 at 50° gives a constant which differs widely from the remaining constants at this temperature. No explanation is known for this discrepancy. The probable error of the average constant at 50°, if this value is excluded, is about equal to the probable error introduced by the probable errors in the measured pressures of nitrosyl chloride, while if this value be included the probable error of the average equilibrium constant is increased three-fold. We feel therefore that this value should likewise be excluded in obtaining an average equilibrium constant. When these values are excluded the average value of $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$.

Evidence of a True Equilibrium.—We may present the following evidence that a true equilibrium free from side reactions has been obtained. The data of Table III show that the equilibrium constant is independent of the direction from which the equilibrium is established. It is independent of moderate variations in the partial pressure of the starting materials. No light-absorbing gas other than nitrosyl chloride or methyl nitrite (such as nitrogen dioxide) is likely to be present in appreciable amounts since the calculated concentration of nitrosyl chloride was the same at several wave lengths and any other absorbing gas would not likely have a characteristic absorption curve so very much like nitrosyl chloride. An experiment was carried out in which definite amounts of hydrogen chloride and methyl nitrite were mixed and the calculated pressure was obtained showing that no change in pressure occurred during the reaction. The equilibrium pressure of nitrosyl chloride as determined by its light absorption was found not to be changed on standing in the dark for an hour or on being illuminated for two hours.

Thermodynamic Calculations.—From the equilibrium constants we find for the reaction

$$CH_3ONO\ (g) + HCl\ (g) = CH_3OH\ (g) + NOCl\ (g)$$

$\Delta F^\circ_{298.1} = 385$ cal. and $\Delta F^\circ_{323.1} = 182$ cal.

Assuming ΔC_p zero over the range of temperature investigated $\Delta H_{298.1} = 2805$ cal. Then $\Delta S^\circ_{298.1} = 8.12$. The error in ΔF is quite small. The probable error of ΔH may be estimated roughly at 300 to 400 cal. and of ΔS about 1.0 entropy unit.

To calculate $\Delta F^\circ_{298.1}$, $\Delta H_{298.1}$ and $\Delta S^\circ_{298.1}$ for the reaction of formation of methyl nitrite from the elements and the entropy of methyl nitrite it will be necessary to make some choice of the available thermodynamic data of the other three substances occurring in the equilibrium. We have chosen the following data

$$\tfrac{1}{2}H_2\,(g) + \tfrac{1}{2}Cl_2\,(g) = HCl\,(g) \quad \Delta F^\circ_{298.1} = -22740^4$$
$$NO\,(g) + \tfrac{1}{2}Cl_2\,(g) = NOCl\,(g) \quad \Delta F^\circ_{298.1} = -4300 \quad \Delta H_{298.1} = -9300^5$$
$$\tfrac{1}{2}N_2\,(g) + \tfrac{1}{2}O_2\,(g) = NO\,(g) \quad \Delta H_{298.1} = 21600^6$$
$$CH_3OH\,(l) + 3/2O_2\,(g) = CO_2\,(g) + 2H_2O\,(l) \quad \Delta H_{298.1} = -173{,}630^7$$
$$C\ (\text{graphite}) + O_2\,(g) = CO_2\,(g) \quad \Delta H_{298.1} = -94240^8$$
$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) = H_2O\,(l) \quad \Delta H_{298.1} = -68313^9$$

Vapor pressure of CH_3OH (l) at 298.1° = 122.2 mm.[10]

$$CH_3OH\,(l) = CH_3OH\,(g) \quad \Delta H_{298.1} = 8947^{11} \quad \Delta S^\circ_{298.1} = 26.36$$

The following values of the molal entropy at $T = 298.1°$ and one atmosphere have been used for third law calculations

H_2 (g) = 31.23	Giauque, THIS JOURNAL, **52,** 4825 (1930)
C (graphite) = 1.3	Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 464
N_2 (g) = 45.78	Giauque, private communication
O_2 (g) = 49.03	Giauque and Johnson, THIS JOURNAL, **51,** 2300 (1929)
Cl_2 (g) = 53.3	McMorris and Yost, *ibid.*, **53,** 2625 (1931), footnote 2631
NO (g) = 50.43	Johnson and Giauque, *ibid.*, **51,** 3194 (1929)
HCl (g) = 44.64	Giauque and Wiebe, *ibid.*, **50,** 101 (1928)
CH_3OH (l) = 30.3	Kelley, *ibid.*, **51,** 180 (1929)

The resulting data for the free energy, heat and entropy of formation at 298.1° and one atmosphere and the entropy of the four substances occurring in the equilibrium are listed in Table IV.

[4] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1930, Vol. VII, p. 233.

[5] Dixon, *Z. physik. Chem.*, Bodenstein Festband, p. 679, July 15 (1931).

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 560.

[7] Rossini, *Proc. Nat. Acad. Sci.*, **17,** 343 (1931).

[8] Roth and Naeser, *Z. Electrochem.*, **31,** 461 (1925).

[9] Rossini, *Bur. Standards J. Research*, **6,** 1 (1931).

[10] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. 3, p. 216.

[11] Fiock, Ginning and Holton, *Bur. Standards J. Research*, **6,** 881 (1931).

TABLE IV

CONSTANTS AND DATA FOR COMPOUNDS

	HCl (g)	NOCl (g)	CH_3OH (g)	CH_3ONO (g)
$\Delta F^\circ_{298.1}$	−22,740	16,400	−38,870	−100
$\Delta H_{298.1}$	−22,030	12,300	−48,290	−16,750
$\Delta S^\circ_{298.1}$	2.38	−13.8	−31.6	−55.9
$S^\circ_{298.1}$	44.64	60.3	56.7	64.2

Summary

Quantitative measurements of the light absorption of nitrosyl chloride and methyl nitrite have been made. Measurements of the light absorption due to nitrosyl chloride present in the gas phase equilibrium CH_3ONO (g) + HCl (g) = CH_3OH (g) + NOCl (g) have been made and equilibrium constants calculated for the temperatures of 25 and 50° for both the forward and reverse reactions. The equilibrium is instantly established, is independent of the direction from which it is established and is free from side reactions. The equilibrium constants are $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$. From these values and from thermodynamic data in the literature for hydrogen chloride, nitrosyl chloride and methyl alcohol we have calculated the free energy, the heat and the entropy of formation and the entropy of methyl nitrite.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

REACTION OF GASES WITH INCANDESCENT TANTALUM

BY MARY R. ANDREWS

RECEIVED DECEMBER 19, 1931 PUBLISHED MAY 7, 1932

It has been known for many years that tantalum, when heated, absorbs actively such gases as nitrogen and hydrogen, but early experimentation was confined to the comparatively low temperatures obtainable in furnaces, and the pressures were the comparatively large ones measurable with a manometer.[1] With modern methods of vacuum technique, it is possible to study reactions at very low pressures and at temperatures up to the melting point of the material under observation. Tantalum offers a particularly interesting subject for such a study.

The following work was done with tantalum filaments mounted in bulbs on an exhaust system. The system contained a reservoir of the particular gas in use and suitable mercury traps for shutting off known volumes. Pressures were read with McLeod gages.

[1] Von Bolton, *Z. Electrochem.*, **11**, 45 (1905); Sieverts and Bergner, *Ber.*, **44**, 2394 (1911); Balke, *Chem. Met. Eng.*, **27**, 1271 (1922); Borelius, *Metallwirtschaft*, **8**, 105–108 (1929)

Nitrogen.—The tantalum filament was given a preliminary degassing in vacuum at 2400–2500° until the cold resistance had decreased to a constant value and no more gas was evolved. A known pressure of nitrogen was then admitted, the filament run at a constant wattage and the pressure was read at known intervals until the gas had been absorbed to an equilibrium pressure.

If, now, another charge of nitrogen was admitted and the filament again run, absorption took place at a somewhat lower rate than before, and the equilibrium pressure was somewhat greater (see Fig. 1). During the first part of any run, the temperature is uncertain, due to the cooling effect of the gas, but for low equilibrium pressures the temperature at the end of the run is accurate within a few degrees.

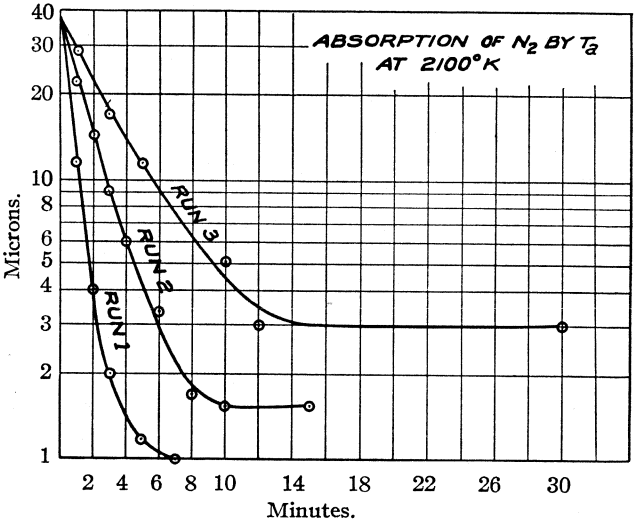


Fig. 1.—Absorption of nitrogen in a volume of 3250 cc. by a 10 mil tantalum filament 20 cm. long at 2100°K. Pressure in system *vs.* time of absorption.

If, after absorbing nitrogen, a filament is run in an evacuated bulb, it will evolve gas until an equilibrium pressure is again reached. For a given concentration of gas in the metal, the equilibrium at any given temperature is the same whether obtained by absorption or evolution. If the filament is heated while the gas evolved is steadily pumped away, it will lose all the nitrogen it has absorbed and return to its original degassed condition. In this process there is no loss of tantalum.

These results prove that, at least in low concentrations, nitrogen goes into tantalum by solution, not by the formation of a compound. Were a compound formed, the equilibrium pressure (or decomposition pressure) would be constant during absorption at any given temperature, inde-

pendent of the amount absorbed, until all the metal had been converted to the compound.

Figure 2 shows a composite curve of the logarithm of the equilibrium pressure *versus* the logarithm of the concentration of nitrogen in the filament at 2240°. The concentration is given as the volume (at N. T. P.) of gas absorbed divided by the volume of the filament, that is, the number of times its own volume absorbed by the filament. It should be noted that the slope is about 1:2, or that the pressure varies as the concentration squared. This agrees with results obtained by Sieverts and Bergner on the

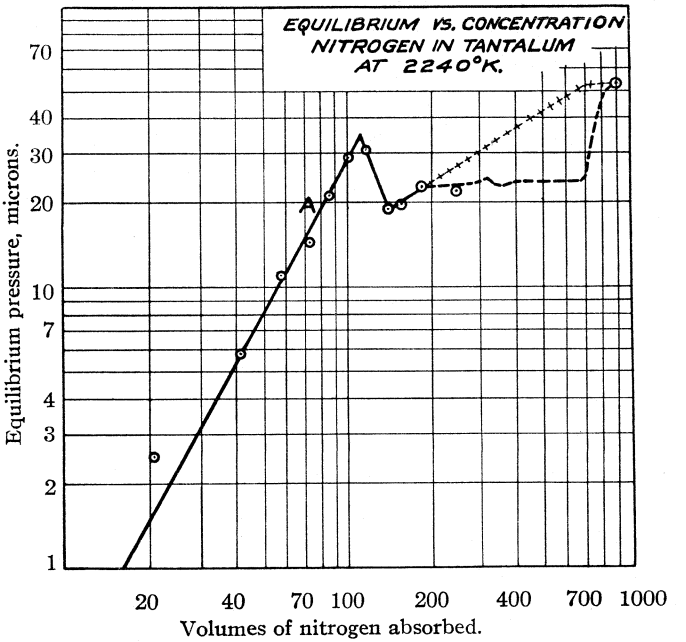


Fig. 2.—Equilibrium pressure *vs.* concentration of nitrogen in tantalum at 2240°K.

solubility of *hydrogen* in tantalum, and indicates that the gas is absorbed in the atomic state. At a concentration of about a hundred volumes, which would give a composition corresponding to $Ta_{10}N$, this curve shows a sudden break in such a direction that by increased concentration of nitrogen in the filament the equilibrium pressure is lowered. Dr. W. P. Davey very kindly took x-ray photographs of two samples of nitrogen-charged tantalum, one of which contained about fifty volumes of nitrogen, the other about two hundred volumes. The first filament showed only the tantalum structure, but the second, more highly charged filament, showed, besides the tantalum structure, an entirely different crystal form. It is not known whether this is the structure for tantalum nitride or whether the

strain produced by the absorbed gas causes the metal to go into a new form in which nitrogen is more soluble. If the change is to the nitride structure, one would assume that the decomposition pressure of the compound was about that at the point A (Fig. 2) and that the metal in absorbing nitrogen became supersaturated and then suddenly reacted to form the nitride with the excess gas, both within and without the metal. This would explain the shape of the curve at higher concentrations quite nicely, the level part at more or less constant equilibrium pressure being the range through which nitride is being formed. There are, however, objections to this theory. First, it is possible to produce this maximum not only through absorption, but also in the opposite direction by evolution of gas from the filament. For instance, a filament which had absorbed 275 volumes of nitrogen was heated at 2200°K. in an evacuated system of known volume so that it evolved gas until an equilibrium pressure was reached. Gas was pumped out and equilibrium again obtained by evolution from the filament. The following shows the maximum pressure obtained at 112 volumes of nitrogen in the filament

Vol. of N_2 in filament.....	200	175	112	70
Equilibrium pressure, microns.....	23	22	35	26

If the peak were due to supersaturation, it should not appear when the gas is removed. Moreover, the electrical resistance at room temperature, which increases almost linearly with the concentration of nitrogen, shows no break at this critical concentration, such as would be expected if a compound were being formed [see Fig. 4].

As for the shape of the pressure–concentration curve obtained at the higher concentrations (shown as a broken line in Fig. 2), it may have to be altered considerably because above a concentration of about 200 volumes the emissivity of the surface appears to increase gradually, the color going to a dull gray. As no allowance was made for this change, in the wattages used, the filament temperature undoubtedly fell considerably through the range 200 to 700 volumes concentration. Above seven hundred volumes the equilibrium pressure appears to increase rapidly, but because at these high concentrations the filament becomes very brittle, few measurements could be made. A concentration of 900 volumes would correspond to complete conversion of the metal to TaN. It seems probable, therefore, that at about the concentration of 700 volumes this compound begins to form with a resulting sintering of the surface and a rise of the temperature to something much closer to the original value. If this is so the equilibrium curve should follow, at constant temperature, the cross-hatched line shown in Fig. 2.

As the temperature of the metal is increased, the rate of solution increases, but the solubility decreases, *i. e.*, the equilibrium pressure for any

given concentration increases. Absorptions were made from 1600 to 2400°K. Figure 3 shows the equilibrium pressures for constant nitrogen content in the wire, plotted as the logarithm of the pressures against the inverse of the temperature. From the slope of these lines, the heat of solution is calculated to be 102,000 calories. This value may be somewhat in error due to the necessary correction made for the cooling effect of the gas on the filament at the higher temperatures and pressures.

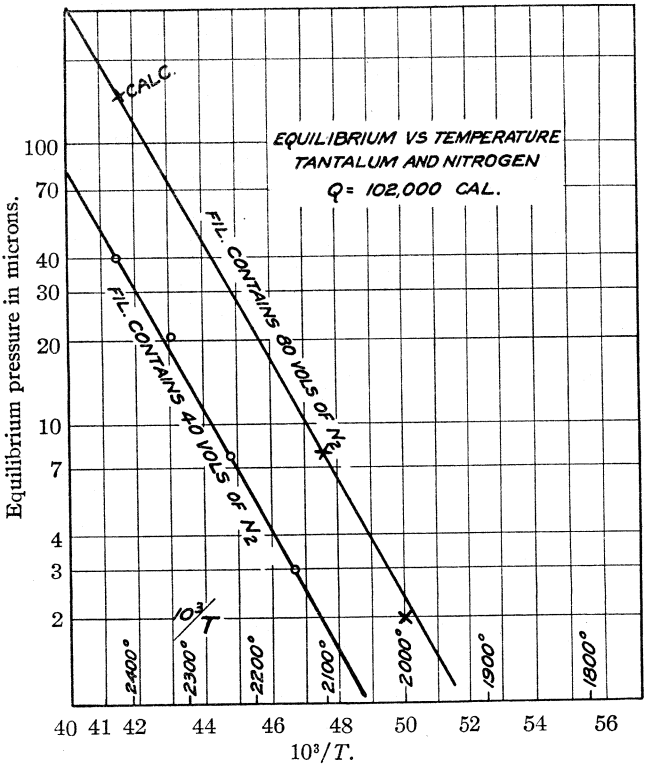


Fig. 3.—Equilibrium pressure *vs.* temperature at constant concentration of nitrogen. Lower curve: filament contains 40 volumes of nitrogen. Upper curve: filament contains 80 volumes of nitrogen.

Oxygen.—Oxygen is absorbed by tantalum in a somewhat different manner than nitrogen. Whereas nitrogen is taken up very slowly below 1600°, oxygen is absorbed quite readily at 1000°K. and with extreme rapidity at 1800°. Absorption is quite complete up to twenty volumes, the residual pressures being negligible. Further absorption at 1800° (which takes place with great rapidity) leads to the formation of a compound. This is shown by the variation of the resistance with gas content.

(See the oxygen curve in Fig. 4.) The cold resistance increases rapidly with concentration up to twenty volumes and then much more slowly. There appears to be a slight supersaturation just before the oxide begins to form. Not enough work has been done in the absorption of oxygen to show whether the solubility, at the point at which compound formation begins, varies with temperature.

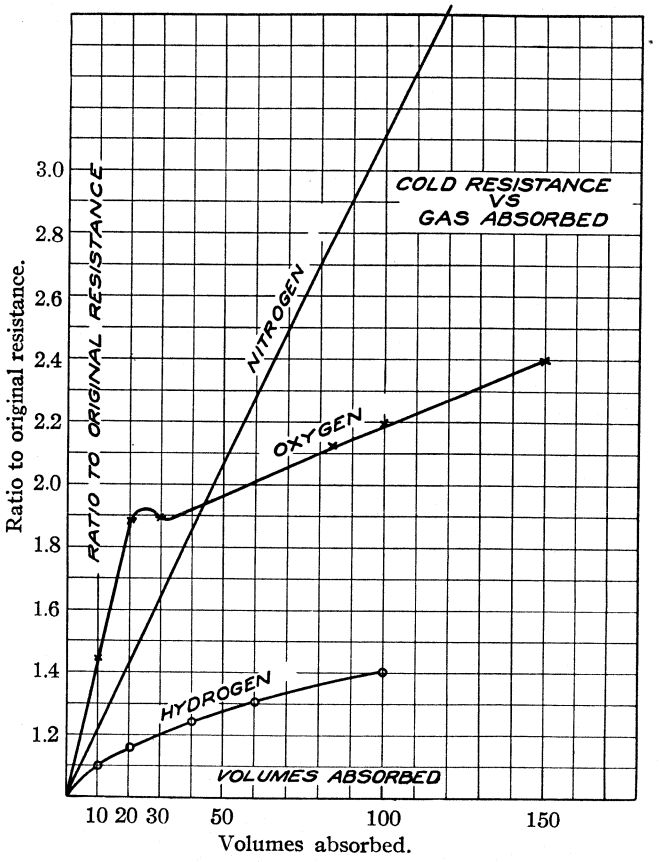


Fig. 4.—Resistance at room temperature *vs.* gas content. Resistance given as the ratio to the resistance of the gas-free filament.

A filament containing twenty volumes of oxygen was examined by Dr. Davey with the x-ray spectrograph. It showed the tantalum structure, but the lattice was stretched, apparently somewhat more in one direction than in the others. This would be exactly what might be expected from a solution of gas in the metal.

Microphotographs were taken of longitudinal sections of a filament that had absorbed 500 volumes of oxygen. The filament was very badly

crinkled and the surface under the microscope looked cracked and scaly (see Fig. 5). The photographs show that penetration takes place most freely along grain boundaries so that the oxide forms in streaks and thin sheets. A concentration of 500 volumes is about one-fifth that necessary to form Ta_2O_5, and the photographs suggest that nearly this fraction of the metal has reacted.

At the point at which the oxygen compound is first formed, the filament begins to turn dark, so that temperatures were quite uncertain at higher concentrations.

The dissolved oxygen, *i. e.*, the first twenty volumes absorbed can be re-evolved if the filament is run in vacuum at 2200–2300°. There is no appreciable loss of metal in the process. If a filament containing a greater amount of oxygen is heated to such a temperature, some metal is vaporized and deposits as a black film on the bulb wall.

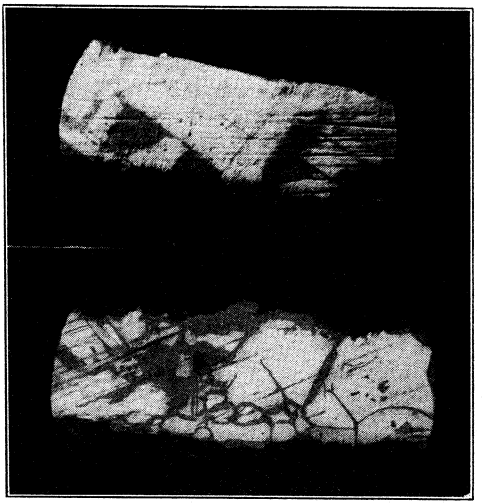


Fig. 5.—Photomicrographs of tantalum filament which has absorbed 500 volumes of oxygen.

Hydrogen.—The absorption of hydrogen offers an interesting study. At the pressures used, 50 microns or less, no hydrogen was absorbed when the tantalum was heated in the gas; but if an auxiliary filament of tungsten was run in the same bulb at a high temperature so as to dissociate some of the hydrogen and the tantalum filament was run at the same time at 800 to 1200°, hydrogen was absorbed by the tantalum. Solubility was greater at the lower temperatures. At any given temperature absorption would take place until an equilibrium was established. Addition of more hydrogen caused increased absorption. The action was exactly similar to the absorption of nitrogen except that equilibrium was established between the dissolved hydrogen and the external pressure of *atomic* hydrogen. That is, if equilibrium was established with the tungsten filament running at a constant temperature, say 2400°K., and the tantalum also constant, at say 1000°K., and the temperature of the tungsten filament was then increased, to, say, 2600°, thus increasing the fraction of the hydrogen dissociated, the tantalum absorbed hydrogen further until a new equilibrium was established. If the tungsten filament was lowered in temperature, the tantalum would immediately evolve gas to

establish again an equilibrium, or if the current was taken off the tungsten filament, the tantalum one being left at 1000°K., gas would be evolved from the tantalum until practically all that had been absorbed had reappeared.

The hydrogen curve in Fig. 4 shows that the resistance at room temperature rises less rapidly with hydrogen concentration than for either oxygen or nitrogen. It can be assumed that this is due to the small atomic volume of the hydrogen, so that a given number of molecules dissolved in the metal would strain the lattice less than larger atoms. There was no evidence of any compound up to the maximum concentrations of hydrogen reached.

Water Vapor.—One or two experiments were made on the reaction between water vapor and hot tantalum. Above 1400°K. the water is decomposed with absorption, by the filament, of the oxygen and evolution of the hydrogen. At 1200° the reaction is negligibly slow.

It was observed in the absorption of both nitrogen and hydrogen that the rate of absorption was much less when a new filament was used than it was after the filament had absorbed gas and had been degassed. Rates were never constant, however. This suggests that diffusion of these two gases as well as of oxygen takes place along grain boundaries and that gassing and degassing helped to open up the structure so that diffusion was more rapid than when the filament was new.

Hydrocarbons.—When heated between 2000 and 2800°K. in low pressures of hydrocarbon vapors, such as benzene or naphthalene, tantalum can form two carbides. The first one to form, *i. e.*, the one of lowest decomposition pressure, is silvery-gray and has a chemical composition of Ta_6C_5. The electrical resistivity of this carbide is about twelve times that of pure tantalum, or 180×10^{-6}, and the temperature coefficient of resistance is very low. Our measurements do not permit of great accuracy in this determination since by complete conversion to this compound the filament is often warped and sometimes shows longitudinal cracks, but the above figure should be accurate to within 20%. This value agrees with the resistivity and temperature coefficient reported by Friedrich and Sittig,[2] and copied elsewhere for the compound TaC.

If the filament is heated further in hydrocarbon vapor, the electrical resistance decreases due to the formation of the compound TaC. This has a resistivity about 120% that of pure tantalum, or a specific resistivity of 17 to 18×10^{-6}. TaC has a brilliant golden-yellow color when in the dense crystalline form and shows a metallic luster equal to that of well-crystallized metals. Both carbides have high melting points, certainly above 3800°K., but no determinations of the two in the pure state have been made here. It would appear, however, from the color and electrical resistivity of their material that Friedrich and Sittig[2] found the melting point of Ta_6C_5 (rather than TaC as they report) to be 4000–4100°K. The

[2] Friedrich and Sittig, *Z. anorg. allgem. Chem.*, **144**, 169–189 (1925).

material used by Agte,[3] which he found to have a melting point of 4150 ± 150°K., was almost certainly TaC at the start and probably suffered only superficial decarbidization during the melting point determination.

When formed from metal by diffusion of carbon inward, as when a tantalum filament is heated in hydrocarbon vapor, the rate of formation is very much less than is the case when tungsten is carbidized in the same way. The time necessary to convert a 10 mil tantalum filament to the first carbide, Ta_6C_5 at 2600°K., for instance, is fully ten times as great as that for conversion of a similar filament of tungsten to the carbide W_2C. Like the two carbides of tungsten, both tantalum carbides are brittle. They have been prepared also in powder form by the well-known method of heating mixtures of tantalum oxide and carbon in hydrogen protected by graphite boats. The products agree in composition with those formed by carbidizing metallic filaments. The colors of the powdered materials are, for Ta_6C_5, a dark gray, and for the TaC a yellowish-brown.

When a filament of the yellow TaC is heated to 2500°K. or more in vacuum or in a neutral gas, such as argon, it loses carbon at a rate depending on the temperature and gas pressure. If the heating is interrupted from time to time to measure the cold resistance, the latter is found to increase very greatly until it has reached the resistance of the compound Ta_6C_5. On further heating, if this be kept below the temperature at which metallic tantalum melts, the loss of carbon continues and the resistance decreases until that of a pure tantalum filament is reached. If the temperature of the carbidized filament is above the melting point of tantalum, fusion occurs as soon as an appreciable amount of the Ta_6C_5 has lost carbon to form a small amount of tantalum, and the filament burns out immediately. In the decomposition of TaC to Ta_6C_5 even at temperatures of 3000 to 3400°K. there is no appreciable evaporation of the tantalum, or of the carbides.

In conclusion I take this opportunity for thanking Dr. Saul Dushman for his interest and advice and Mrs. Donald McLeod for her assistance in making these investigations.

Summary

A study has been made of the behavior of filaments of tantalum when heated in low pressures of nitrogen, hydrogen, oxygen or hydrocarbons. In nitrogen, absorption increases with increased pressure until about 100 volumes are absorbed. At this point the equilibrium pressure drops as absorption increases. Absorption can take place to the formation of TaN. In hydrogen, the amount absorbed depends on the concentration of atomic hydrogen in the gas. In oxygen, absorption followed by oxide formation

[3] Agte, Dissertation, Technische-Hochschule zu Berlin, April 8, 1931. Agte and Alterthum, *Z. anorg. allgem. Chem.*, **144**, 169–189 (1925).

occurs. In hydrocarbons, two carbides may be formed—Ta_6C_5 and TaC. These both have very high melting points. The former has a specific resistance of about 180×10^{-6}, the latter of about 18×10^{-6}.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. VII. THE CARBON VALENCE ANGLE

BY C. P. SMYTH AND W. S. WALLS

RECEIVED DECEMBER 21, 1932 PUBLISHED MAY 7, 1932

The experimental examination of the angle between the valences of the carbon atom may seem an attempt to prove the obvious, but the calculations of Slater[1] and of Pauling[2] by means of wave mechanics that the angle is the regular tetrahedral valence angle, 109.5°, and the evidence as to the angle given by x-ray[3] and electron scattering[4] in gases make it desirable to extend the preliminary application of electric moments which has been made in the study of the problem.[5] This preliminary application was made in the case of the moments of the halogenated methanes. Rough kinetic theory diameters were calculated for chlorine, bromine and iodine by comparison with the dimensions of the corresponding inert gas structures and used as the internuclear distances of the halogens in the methylene halides. The assumption of these distances, when used with the carbon–halogen nuclear separations obtained by Pauling,[6] necessitated a widening of the angle between the C–X valences to 124° in methylene chloride, 120° in methylene bromide and 135° in methylene iodide. When the C–X dipole moments were resolved at these angles, the resultants agreed so well with the experimentally determined moments of the molecules that the moments were regarded as indicating these values for the angles between the C–X valences. However, it was stated that the disregard of the inductive effects of the dipoles as well as the speculative nature of the treatment of the atomic dimensions rendered the excellence of the agreement between the observed and the calculated values of the moments somewhat fortuitous. As the inductive action of each C–X dipole in the methylene halide lowers the moment of the other C–X dipole in the molecule, it is evident that the angle calculated between the dipoles without regard for this effect is too large, although it is interesting to note that the recent calculation by Bewilogua[3] from the results of x-ray scattering also

[1] Slater, *Phys. Rev.*, **37**, 481 (1931); *ibid.*, **38**, 1109 (1931).

[2] Pauling, THIS JOURNAL, **53**, 1367 (1931).

[3] Debye, *Z. Elektrochem.*, **36**, 612 (1930); Bewilogua, *Physik. Z.*, **32**, 265 (1931).

[4] Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

[5] Smyth and Rogers, THIS JOURNAL, **52**, 2227 (1930).

[6] Pauling, *Z. Krist.*, **67**, 377 (1928).

gives 124° for the angle between the C–Cl valences in methylene chloride. As it appears impossible, at present, to calculate satisfactorily the lowering of the moments by induction, this complication has been avoided by removing the component dipoles so far from one another in the molecule as to render their mutual inductive effects negligible.

In the separation of the dipoles from one another advantage is taken of the fact that the valences directed outward from a benzene ring act in the plane of the ring so that para valences act in the same straight line in opposite directions.[7] Instead, therefore, of methylene compounds, para-substituted benzyl compounds as represented in Fig. 1 have been measured. In support of this procedure, not only the zero moments of *p*-dinitrobenzene, and *p*-dichloro-, *p*-dibromo- and *p*-diiodobenzene may be cited, but also the excellent agreement of the observed and calculated values when different groups are in the para positions. Thus, the electric moment of nitrobenzene is 3.9×10^{-18} [8] and that of chlorobenzene 1.52×10^{-18}. As the two dipoles should act in opposite directions in the same straight line in *p*-chloronitrobenzene, the resultant moment should be $(3.9 - 1.52) \times 10^{-18} = 2.38 \times 10^{-18}$, in excellent agreement with the observed value 2.45×10^{-18}. If the bromine moment 1.50×10^{-18} is substituted for the chlorine, the calculated value is 2.40×10^{-18} and the observed 2.53×10^{-18}. The results are a little less satisfactory in the case of the cyanides. As the moment of benzonitrile is indistinguishable from that of nitrobenzene, one would expect zero moment for *p*-nitrobenzonitrile, but the observed value is 0.7×10^{-18}. The moment of *p*-bromobenzonitrile should be $(3.9 - 1.50) \times 10^{-18} = 2.4 \times 10^{-18}$, while the observed value is 2.64×10^{-18}. For *m*-nitrobenzonitrile, in which the two dipoles should make an angle of 120° with each other, the moment should be 3.9×10^{-18}, and the observed value is 3.8×10^{-18}. As the agreement between the observed and calculated values for these two latter compounds is satisfactory and as the small moment apparently observed for *p*-nitrobenzonitrile may be due entirely to the effect of neglected atomic polarization, it seems justifiable to treat the moment

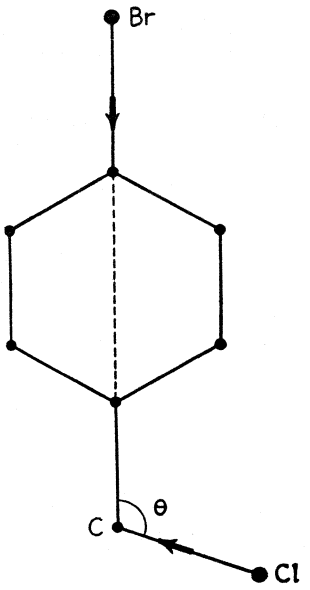


Fig. 1.—The *p*-bromobenzyl chloride molecule.

[7] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931, Chap. VI.

[8] The values of moments, for which the experimental data are not given in this paper, are taken from the appendices of "Dielectric Constant and Molecular Structure."

associated with the cyanide group as acting in the direction of the line joining the group to the rest of the molecule. This implies that the carbon and nitrogen nuclei are in line with the nucleus of the carbon atom to which the group is attached, and is consistent with Pauling's conclusion that the HCN molecule is linear.[2]

A question may be raised as to the effect of the moments of the two principal dipoles upon each other It has been shown that carbon–halogen dipoles exert an inductive effect, detectable in the observed moments, through only two carbon atoms of a saturated chain,[5] while the larger cyanide dipole has a measurable effect upon the third atom of the chain, but would affect the fifth to a hardly detectable extent.[9] Since, in the para-substituted benzyl compounds, the principal dipoles are separated by five carbon atoms it may be concluded that the moments of these dipoles would little affect one another. This is supported by the values of the moments of *p*-chloro- and *p*-nitrotoluene. As the moment of the toluene molecule, 0.4×10^{-18}, is regarded as acting in the direction of the line joining the methyl carbon to the ring with its positive end toward the former, the moment of *p*-chlorotoluene should be $(0.4 + 1.52) \times 10^{-18} = 1.92 \times 10^{-18}$ and that of *p*-nitrotoluene should be $(0.4 + 3.9) \times 10^{-18} = 4.3 \times 10^{-18}$. As the two dipoles point in the same direction in each of the two molecules, the moment of each should be increased if there were any appreciable inductive action between them, but the observed moment of the one is 1.74×10^{-18} and of the other 4.50×10^{-18}, differing from the calculated values by no more than the possible error. It would thus appear that the moments of the two principal dipoles may be regarded as approximately independent of each other.

A final question may be raised as to whether it is justifiable to treat the moment of a molecule such as benzyl chloride as acting in the C–Cl line, *e. g.*, in the diagram of the *p*-bromobenzyl chloride molecule in Fig. 1, can the dipoles be represented merely by the two arrows shown, the effects of the C–H bonds and of the attachment of the $-CH_2Cl$ group to the ring being neglected? Unfortunately, we do not know the small moment, if any, associated with the C–H bond, for the arbitrary calculation of it by Eucken and Meyer[10] as 0.4×10^{-18}, though useful for some purposes, cannot be regarded as establishing its value. The moment of methyl chloride, 1.86×10^{-18}, must act in the line joining the carbon and chlorine nuclei. When one of the hydrogens is replaced by a methyl group to form ethyl chloride, the moment increases by 0.15×10^{-18} because of the moment induced in the added methyl group. It has been seen that, in toluene, a moment of 0.4×10^{-18} acts in the direction of the line joining the methyl carbon to the ring with its positive end toward the methyl carbon.

[9] Smyth, "Dielectric Constant and Molecular Structure," p. 99.

[10] Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

In benzyl chloride a moment of about the same magnitude should occur in about the same location and should oppose the induced moment, as the induced dipole would have its positive end toward the ring. If the carbon valence angle is about 110°, the projection of what may be called the toluene moment, 0.4×10^{-18}, in the direction of the principal moment is 0.14×10^{-18}. In other words, the toluene moment is of such a size as to cancel approximately the increase in induced moment accompanying the replacement of a methyl hydrogen by a phenyl group, which is borne out by the agreement of the moment of benzyl chloride, 1.85×10^{-18}, with that of methyl chloride. The representation of the benzyl chloride moment by a single arrow in the C–Cl line appears, therefore, to be a justifiable approximation, and the similar representation of the moment produced by substitution of the bromine on the ring in Fig. 1 is certainly correct. Identical reasoning should apply to benzyl bromide and its substituted products, but uncertainty in the value for the moment of methyl bromide and the effect of atomic polarization upon the values for the higher alkyl bromides makes the reasoning inconclusive. However, the moment of benzyl bromide, 1.86×10^{-18}, is lower than that calculated for ethyl bromide without taking into account the atomic polarization by an amount identical with the difference between benzyl chloride and ethyl chloride. The moment of benzyl cyanide, 3.52×10^{-18}, is 0.3×10^{-18} higher than that of methyl cyanide, as might be expected from the greater inductive effect of the large cyanide dipole, which the toluene moment is not large enough to cancel. This small induced moment can, as an approximation, be treated as acting in the direction of the C–CN line and is, of course, included in the value 3.52×10^{-18} for the molecule. Evidently it is a justifiable approximation to treat the moment of a $C_6H_5CH_2X$ molecule as acting in the C–X line and Fig. 1 may be regarded as an approximately correct representation of the moments. It is also evident that the larger the moments of the two principal dipoles, the smaller will be the relative effects of the approximations and neglected factors and the greater the accuracy of the value calculated for the valence angle θ.

Preparation of Materials

Benzene.—Merck's C. P. benzene was shaken with concentrated sulfuric acid until no coloration appeared, washed with water, with dilute sodium carbonate solution, and three times with water, dried over calcium chloride, twice fractionally crystallized, refluxed over phosphorus pentoxide and fractionally distilled, refluxed over sodium wire and distilled; b. p. 80.2–80.3° (757 mm.); n_D^{20} 1.50135; n_D^{25} 1.49815.

Heptane.—Material from the Ethyl Gasoline Corporation was fractionally distilled from phosphoric anhydride; b. p. 98.2–98.3° (757 mm.); n_D^{20} 1.38775; n_D^{25} 1.38530.

All the remaining materials were obtained from the Eastman Kodak Company.

Benzyl Bromide.—Material (b. p. 80–83°, 10 mm.) was fractionally distilled under reduced pressure, the fraction distilling at 86.8–87.5° (19 mm.) being collected. This fraction was redistilled; b. p. 87.0–87.2° (19 mm.); d_4^{25} 1.4324.

Benzyl Cyanide.—Material (b. p. 98–100°, 8 mm.) was twice fractionally distilled under reduced pressure; b. p. 115.2–115.4° (19 mm.); n_D^{20} 1.52327; n_D^{25} 1.52086; d_4^{25} 1.0119; d_4^{50} 0.9914. A sample distilled from phosphoric anhydride had the same n_D^{20}.

***p*-Bromobenzyl Chloride.**—Material (m. p. 40–41°) was fractionally distilled under reduced pressure (b. p. 118–119°, 16 mm.), fractionally crystallized from petroleum ether, dried in a vacuum desiccator and twice fractionally crystallized; m. p. 41.3–41.5°.

***p*-Chlorobenzyl Bromide.**—Material (m. p. 48.5–49°) was twice fractionally crystallized from petroleum ether and dried in a vacuum desiccator; m. p. 48.5–48.7°.

***p*-Nitrobenzyl Bromide.**—Material (m. p. 98–99°) was twice fractionally crystallized from a mixture of dry benzene and petroleum ether, washed with petroleum ether and dried in a vacuum desiccator; m. p. 99.4–99.7°.

***p*-Nitrobenzyl Chloride.**—Material (m. p. 70–71°) was fractionally crystallized from carefully dried ether and dried in a vacuum desiccator; m. p. 71.2–71.5°.

***p*-Nitrobenzyl Cyanide.**—Material (m. p. 116°) was twice fractionally crystallized from dry benzene, washed with petroleum ether and dried in a vacuum desiccator; m. p. 116.6–116.8°.

Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the non-polar were measured with the apparatus and methods previously employed,[11] a wave length of 1000 meters being used in the dielectric constant determinations. In Table I the first column gives the mole fraction c_2 of the polar substance in the heptane or benzene solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ and the densities d of the solutions and the polarizations P_2 of the polar substance. P_2 is calculated by means of the usual equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The molar refraction for the D sodium line, MR_D, of benzyl bromide has been calculated from the atomic refractions given in Landolt–Börnstein (fifth edition), that of benzyl cyanide has been determined directly, and the values for the other substances have been calculated from measurements upon the solutions by means of equations analogous to those for P_{12} and P_2. These values have been used together with those for P_∞, the polarization obtained by extrapolating the P_2–c_2 curve to infinite dilution, and the absolute temperature T to calculate the electric moment μ by means of the equation

$$\mu = 0.0127 \times 10^{-18}\sqrt{(P_\infty - MR_D)T}$$

The absolute values of the moments are a little high because of the neglect of the atomic polarization P_A. The values of the molar refraction and of the orientation polarization $P_\infty - MR_D$ and the moment calculated from the data at 25° and at 50° are listed in Table II, the solvent in which the compound was measured being given in the second column.

[11] Smyth and Walls, THIS JOURNAL, **53**, 527 (1931).

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Benzene–Benzyl Bromide			
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01085	2.332	2.275	.8817	.8546	108.7	104.2
.03019	2.427	2.360	.8957	.8682	106.8	102.6
.03526	2.453	2.383	.8998	.8723	106.4	102.2
.05612	2.555	2.475	.9150	.8875	104.9	100.9
.06180	2.582	2.499	.9190	.8915	104.4	100.5
.10706	2.801	2.696	.9513	.9236	101.6	98.2
			Heptane–Benzyl Bromide			
0.00000	1.920	1.883	0.6795	0.6577	(34.58	35.62 = P_1)
.03132	2.012	1.966	.6988	.6770	109.9	104.9
.04016	2.038	1.989	.7043	.6823	109.3	104.3
.05976	2.097	2.042	.7166	.6944	108.4	103.6
.07896	2.155	2.095	.7288	.7063	107.3	103.0
.12994	2.315	2.241	.7613	.7384	105.3	101.7
.18084	2.493	2.403	.7971	.7737	103.7	100.4
			Benzene–Benzyl Cyanide			
0.00996	2.446	2.376	0.8751	0.8483	274.7	259.7
.01438	2.522	2.443	.8761	.8493	270.1	256.3
.02490	2.698	2.601	.8782	.8515	261.2	248.9
.03031	2.790	2.682	.8792	.8526	257.6	245.2
.03877	2.933	2.809	.8808	.8543	251.4	240.1
.04734	2.076	2.936	.8825	.8561	245.3	234.9
			Heptane–Benzyl Cyanide			
0.00691	1.984	1.941	0.6814	0.6597	289.3	273.4
.01538	2.059	2.010	.6835	.6619	277.8	267.4
.01684	2.072	2.021	.6838	.6621	276.9	265.6
.01978	2.100	2.046	.6846	.6630	276.8	264.6
.02638	2.157	2.098	.6863	.6647	270.0	259.0
.02821	2.170	2.113	.6869	.6652	665.7	258.3
.03115	2.195	2.135	.6876	.6660	263.2	255.1
.04263	2.291	2.226	.6905	.6690	254.2	248.3
.04683	2.325	2.260	.6917	.6702	250.7	246.4
			Heptane–*p*-Bromobenzyl Chloride			
0.02849	1.994	1.951	0.7031	0.6812	102.0	98.5
.04298	2.031	1.985	.7149	.6928	101.1	97.9
.05875	2.072	2.023	.7282	.7059	100.3	97.3
.08259	2.135	2.080	.7475	.7250	99.7	96.5
.09698	2.175	2.118	.7597	.7373	99.5	96.6
			Heptane–*p*-Chlorobenzyl Bromide			
0.02134	1.975	1.934	0.6966	0.6746	103.5	100.7
.03418	2.008	1.964	.7070	.6849	102.5	99.3
.04634	2.039	1.993	.7168	.6945	101.7	98.9
.05775	2.069	2.020	.7260	.7036	101.3	98.3
.07166	2.106	2.054	.7372	.7147	101.0	98.1
.08658	2.146	2.091	.7492	.7267	100.7	97.8

TABLE I (*Concluded*)

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Benzene–*p*-Nitrobenzyl Bromide			
0.00556	2.378	2.318	0.8798	0.8528	300.1	287.6
.00907	2.442	2.375	.8838	.8568	296.8	283.7
.00918	2.443	2.376	.8839	.8569	294.7	282.8
.01333	2.518	2.443	.8886	.8615	291.5	278.9
.01794	2.602	2.517	.8938	.8668	287.6	274.3
.02386	2.711	2.614	.9005	.8735	283.4	270.3
.03314	2.884	2.767	.9108	.8839	277.5	264.9
			Benzene–*p*-Nitrobenzyl Chloride			
0.00741	2.413	2.347	0.8785	0.8516	299.3	281.9
.00880	2.438	2.369	.8795	.8525	297.2	280.2
.01551	2.560	2.477	.8840	.8570	289.8	274.4
.01556	2.561	2.476	.8840	.8570	290.2	273.6
.02530	2.737	2.633	.8904	.8639	281.2	265.9
.03035	2.829	2.714	.8936	.8671	277.1	262.7
.03555	2.926	2.799	.8971	.8706	273.7	259.7
.04185	3.042	2.903	.9013	.8749	269.2	256.2
			Benzene–*p*-Nitrobenzyl Cyanide			
0.00303	2.342	2.287	0.8753	0.8483	346.8	340.3
.00546	2.394	2.334	.8767	.8498	343.6	332.7
.00714	2.430	2.366	.8777	.8508	340.4	329.3
.00736	2.434	2.370	.8778	.8509	339.2	328.4
.01059	2.506	2.433	.8798	.8529	339.3	325.2
.01420	2.587	2.503	.8819	.8551	337.3	320.5
.01555	2.617	2.528	.8827	.8559	336.0	318.1
0.00351	2.354	2.298	0.8755	0.8486	354.3	345.9
.00846	2.463	2.396	.8785	.8516	347.0	335.3
.01053	2.506	2.436	.8797	.8529	341.0	330.7
.01178	2.536	2.460	.8804	.8536	342.5	328.2
.01512	2.611	2.526	.8824	.8556	339.5	324.4

TABLE II

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	Solvent	MR_D	$P_\infty - MR_D$ 25°	$P_\infty - MR_D$ 50°	$\mu \times 10^{18}$ 25°	$\mu \times 10^{18}$ 50°
Benzyl bromide	Benzene	38.69[a]	71.0	66.0	1.85	1.85
	Heptane		73.0	67.0	1.87	1.87
Benzyl cyanide	Benzene	35.22	250.8	232.8	3.47	3.48
	Heptane		262.8	243.8	3.55	3.56
p-Bromobenzyl chloride	Heptane	43.9	61.1	56.6	1.71	1.72
p-Chlorobenzyl bromide	Heptane	44.1	61.4	57.9	1.72	1.74
p-Nitrobenzyl bromide	Benzene	45.2	262.8	245.8	3.55	3.58
p-Nitrobenzyl chloride	Benzene	42.7	266.3	248.3	3.58	3.60
p-Nitrobenzyl cyanide	Benzene	40.8	307.2	300.2	3.84	3.95
			318.2	312.2	3.91	4.03

[a] Calculated value.

Discussion and Interpretation of Results

The moment found for benzyl bromide in heptane is not experimentally distinguishable from that found in benzene solution. In the case of benzyl cyanide, the value found in heptane solution is slightly higher than that in benzene, but, as the low solubility of *p*-nitrobenzyl cyanide in heptane necessitates the use of benzene as solvent, the value for benzyl cyanide found in benzene is used in the calculation of the valence angle, although the mean value 3.52×10^{-18} may be taken for general use as the moment of the molecule. As the moment found for *p*-nitrobenzyl cyanide showed an increase with increase in temperature, a second set of measurements was made upon this substance, the results of which are listed in Tables I and II below those of the first set. The rise with temperature is observed in both sets of measurements, although the agreement is rather unsatisfactory because of the small concentrations of the polar substance necessitated by its low solubility. As no reason for this variation with temperature is apparent in the structure of the molecule,[12] it may possibly arise from incomplete elimination of the effect of intermolecular action by extrapolation of the P_2–c_2 curve. The considerable variation of P_2 with concentration in the very dilute solutions shows the effect of the large dipoles upon one another's orientation, an effect which would be reduced by rising temperature. In view of these circumstances, a value slightly higher than the mean has been adopted for the moment.

The valence angle θ of carbon has been calculated by means of the equation for the resultant μ of two vectors, m_1, and m_2, which make an angle θ with each other. The equation may conveniently be written in the form

$$\cos\theta = \frac{\mu^2 - m_1^2 - m_2^2}{2m_1m_2}$$

In Table III, μ is the moment observed for the molecule of the para-substituted benzyl compound, the formula of which is given in the first column, m_1 is the moment of the unsubstituted benzyl compound, that is, of the C–Cl dipole in Fig. 1, or of one similarly located, and m_2 is the moment of the dipole in the para position. The values are taken from Table II or from the literature.[8]

TABLE III

ELECTRIC MOMENTS ($\times 10^{18}$) AND THE CARBON VALENCE ANGLE

	μ	m_1	m_2	θ
p-$BrC_6H_4CH_2Cl$	1.72	1.85	1.50	119°
p-$ClC_6H_4CH_2Br$	1.73	1.86	1.52	119.5°
p-$O_2NC_6H_4CH_2Cl$	3.59	1.85	3.9	113.5°
p-$O_2NC_6H_4CH_2Br$	3.57	1.86	3.9	114°
p-$O_2NC_6H_4CH_2CN$	4.00	3.48	3.9	114°

[12] *Cf.* Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

The values of the carbon valence angle calculated from the moments of the two para-halogen substituted compounds agree well with one another, as do those calculated from the three para-nitro substituted compounds. The intra-molecular dimensions are such that one would expect little, if any, widening of the valence angle by repulsion between the ring and the side chain. Any such repulsive effect should not be altered by the replacement of a halogen by a nitro group in the para position. It is reasonable to conclude, therefore, that the difference of 5° between the results calculated from the para-halogen substituted compounds and those from the para-nitro is due to the fact that, in the latter, the larger values of the moments render relatively smaller the effects of the approximations necessary in the treatment. As the 4° difference from the theoretical tetrahedral angle may easily arise from these approximations as well as from small errors in μ, m_1 and m_2, it may be concluded that the carbon valence angle determined in these compounds agrees with the theoretical angle of 109°28′ within the limit of the error of experiment and calculation, although, in some cases, the angle may well depart from this value more or less. The results are in excellent agreement with Pauling's estimate of values of 112 and 115° from crystal structure data and with Wierl's calculation from electron scattering that the angle between the C–Cl valences in methylene chloride lies between 110 and 115°. The satisfactory outcome of this treatment establishes the validity of the method, which is now being applied to the determination of the oxygen and sulfur valence angles.

Summary

The electric moments of several benzyl and para-substituted benzyl compounds have been determined and used together with values in the literature to calculate the angle between the valences of the carbon atom. The value obtained, 114°, differs from the theoretical tetrahedral angle by no more than the probable error.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

THE DIELECTRIC CONSTANT OF WATER AND ITS TEMPERATURE COEFFICIENT AS DETERMINED BY A RESONANCE METHOD. II

BY E. P. LINTON[1] AND O. MAASS

RECEIVED DECEMBER 26, 1931 PUBLISHED MAY 7, 1932

In the following a new modification of a dielectric cell is described which makes possible a more accurate determination of the dielectric constant of water by the resonance method than the cell previously used for this purpose.[2]

This cell was also used for the redetermination of the dielectric constants of several liquids and for the measurement of the temperature coefficient of the dielectric constant of water.

New Type of Variable Condenser.—Figure 1 gives a diagrammatic sketch of the new type of cell. It consists of two cylindrical tubes B (closed at each end) and D which are insulated from each other by the glass plates K and C. The outer cylinder D is about 5.2 cm. in diameter and 50 cm. high. By varying the radius of the inner rod a condenser of any desired capacity can be made. In the following measurements two inner tubes were used, one 0.5 cm. and the other 4.4 cm. in diameter.

A maximum of 700 cc. of liquid is necessary to fill the cell. By applying suction or pressure to G the height of the liquid in the cell can be varied as desired, G acting as a reservoir. The position of the liquid in D is measured by means of the glass tube H, which is 2 cm. in diameter. The glass tube F completely filled with liquid is connected through E to D so that the height of the liquid in H is the same as that in D. A, B, E and H are open to the air. A, B, D, G and E are made of pure block tin, and the construction is such that no glass to metal joint is needed in the apparatus.

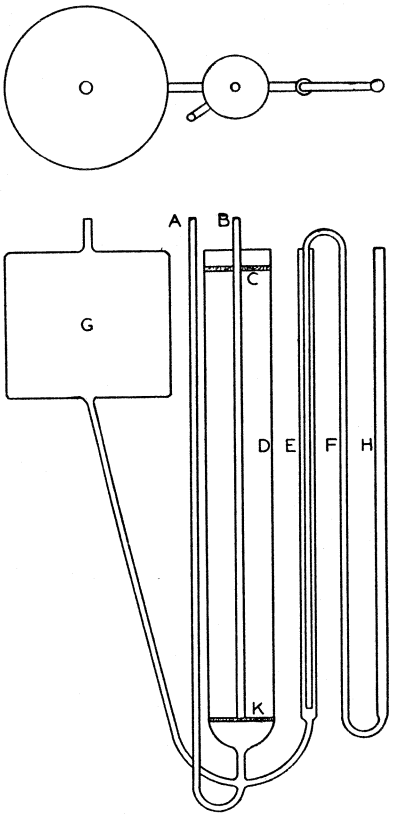


Fig. 1.—The dielectric cell: above, plan; below, elevation,

The purpose of tube A is to drain the liquid from the cell by the application of suction. The cell is dried out by means of a stream of air. As a further precaution the whole apparatus is then rinsed with the liquid whose dielectric constant is to be measured.

[1] Acknowledgment is hereby made of a fellowship granted to one of us by the Research Council of Canada.

[2] Linton and Maass, THIS JOURNAL, **53**, 957 (1931).

The apparatus can therefore be cleaned without dismounting or removal from the thermostat. This enables one to measure a series of liquids without removing the inner tube B. The cell is in convenient form for thermostating. An oil- or water-bath can be used in the thermostat, but the outer cylinder of the condenser must be grounded. Since the capacity of the cell is dependent on the ratio of the radii of the inner and outer tubes, a change in temperature does not alter the capacity of the cell for a fixed height. With the procedure used the cell is therefore admirably adapted for the measurement of a temperature coefficient of a dielectric constant of a liquid over a large range of temperature.

Furthermore, in this cell, since the capacity is dependent on the position of the liquid and not on any setting of condenser plates, complete reproducibility is possible. The capacity of the cell was found to vary in a linear manner within the accuracy to which the height of the liquid in the tube could be read, *i. e.*, to within 0.1%.

Then if ϵ_1 and ϵ_2 are the dielectric constants of two liquids and $C_1 - C_1^1$ and $C_2 - C_2^1$ the corresponding changes of capacity for equal changes in position of the liquids in the cell then

$$\frac{\epsilon_1 - 1}{\epsilon_2 - 1} = \frac{C_1 - C_1^1}{C_2 - C_2^1}$$

These changes in capacity are measured by the tuning condenser as previously described.

To eliminate the influence of conductivity in the case of water at the higher temperatures, the power tube described previously was used. With the above cell the "dead space" was found to be negligible and the linear relationship was given by all intermediate settings of the cell.

Experimental Results

In order to determine the dielectric constant of water it was necessary this time to start with a standard liquid, and benzene was chosen. Smyth evaluates the dielectric constant at 25° as 2.273. The authors have found the value of 2.271. It is considered better, however, to use Smyth's value.

Only two stages are required to determine the dielectric constant of water. In the first, benzene and ethylene dichloride and the 4.4-cm. inner tube was used; in the second, ethylene dichloride and water with the 0.5-cm. inner tube.

The average of five determinations, each of which started with benzene, gave 79.2 as the dielectric constant of water at 25°. The greatest deviation from this mean was one in four hundred. The following dielectric constants for carefully purified liquids were found: ether, 4.23; ethylene dichloride, 10.46; nitrobenzene, 34.9.

Temperature Coefficient of the Dielectric Constant of Water.—A large number of determinations of the dielectric constant of water at various temperatures were made. The procedure was as follows. After filling the cell with pure water the capacity height slope at 25° was determined. Then the cell was brought to a different temperature and the new slope

determined. The cell was filled with fresh conductivity water for each measurement. Occasionally the slope at 25° was redetermined after the temperature change and was always found to be the same. From a series of twenty measurements between 0 and 50°, a smooth curve relating temperature and dielectric constant was drawn. The equation to this curve was found to be

$$\epsilon_t = 79.2(1 - 0.00428(t - 25) + 0.0000212(t - 25)^2 - 0.00000041(t - 25)^3)$$

This equation follows the curve from 0 to 25° with an accuracy of one part in one thousand, from 30 to 50° the accuracy is one in five hundred.

Conclusion

The dielectric constant of water now found is the same as that previously determined by the authors, although the dielectric constants of some of the intermediate liquids are not the same. This difference is due to the greater care taken this time in the purification of the liquids. The purity of the liquid, of course, does not alter the absolute value obtained for the dielectric constant of water as long as the first medium in the series of steps (air or benzene) is pure.

The dielectric constant of water as determined by the authors gives good agreement with the Debye–Hückel theory of ions.[3]

In the Debye–Hückel theory of the heats of dilution of strong electrolytes, the dielectric constant of water and the temperature coefficient of the dielectric constant give much closer agreement with the experimental values found by Lange and Messner[4] than the values obtained by Kockel and Drude. On the basis of Kockel's values, 41 calories, on the basis of Drude's, 33 calories are the calculated values for the heat of dilution of a potassium chloride solution. The authors' value gives 26 calories, which is in fair agreement with 23 ± 3 found by Lange.

The cell as described can be modified as far as dimensions are concerned so as to be available for much smaller quantities of liquids.

Summary

The new type of variable condenser is described which has a greatly increased accuracy as far as setting is concerned. The dielectric constants of water, nitrobenzene, ethylene dichloride, ether and benzene have been measured at 25°. The dielectric constants of water have been measured over the temperature range 0 to 50°. The new values obtained for water were found to be in better agreement with the calculations involved in Debye's theory.

MONTREAL, CANADA

[3] Williams and Brönsted, THIS JOURNAL, **50**, 1342 (1928).

[4] Lange and Messner, *Z. Electrochem.*, **33**, 431 (1927).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 92]

A STUDY OF THE POTASSIUM DITHIO-OXALATE COLORIMETRIC METHOD FOR THE DETERMINATION OF NICKEL

BY JOHN H. YOE AND FLOYD H. WIRSING

RECEIVED DECEMBER 29, 1931 PUBLISHED MAY 7, 1932

Over twenty years ago Jones and Tasker[1] reported a method for making potassium dithio-oxalate, $K_2C_2O_2S_2$. They found that this substance gives intense colors in water solution with certain metallic salts. Among these they discovered that nickel salts give a deep magenta color in dilute solutions. If equal weights of potassium dithio-oxalate and a soluble nickel salt are mixed in concentrated solutions there separate out small black needle-shaped crystals. These crystals color water more intensely than does potassium permanganate.

More recently, Fairhall[2] has employed potassium dithio-oxalate to determine nickel colorimetrically. The reagent is extremely sensitive and thus permits the determination of very small amounts of nickel. Fairhall made determinations on biological materials which contained small known quantities of nickel and obtained results accurate to a fraction of a milligram. His results indicated that potassium dithio-oxalate possessed advantages over other colorimetric reagents for nickel, such as dimethylglyoxime and α-benzyl-dioxime. These advantages are greater sensitiveness and better formation of color.

The purpose of this investigation was to study the reaction between potassium dithio-oxalate and nickel with reference to its use in the colorimetric determination of nickel. The sensitivity of the reaction, application of Beer's law, effect of various ions and different experimental conditions have been studied.

Apparatus and Reagents.—The apparatus and general technique have been described in a paper by Yoe and Hill.[3] A Bausch and Lomb Duboscq colorimeter was used in place of the Kennicott–Campbell–Hurley instrument employed by Yoe and Hill. The Nessler tubes measured 210 mm. to the 50 ml. mark. All weights and volumetric instruments were calibrated.

The potassium dithio-oxalate was obtained from the Eastman Kodak Co. Freshly boiled distilled water was used to make up the reagent solution. A stock solution of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, was prepared and its concentration determined gravimetrically by the dimethylglyoxime method. The average of three closely agreeing results gave 0.9998 g. of

[1] Jones and Tasker, *J. Chem. Soc.*, **95**, 1904–9 (1909).

[2] Fairhall, *J. Ind. Hygiene*, **8**, 528–34 (1926).

[3] Yoe and Hill, THIS JOURNAL, **49**, 2395–2408 (1927).

nickel per liter at 20°. Ten ml. of this solution was diluted to a liter and thoroughly mixed. One ml. of the diluted solution contained 0.01 mg. of nickel and was taken as the standard solution.

Experimental

In the first part of our work a series of eight "unknowns" containing nickel was analyzed. These were checked several times, totaling about 1000 readings for practice in colorimetric measurements with the potassium dithio-oxalate reagent.

The following order of addition of reagents was adopted and observed throughout the investigation. Ten ml. of each of the nickel solutions were pipetted into the colorimeter cups and the required volumes of reagent added according to the concentration of the nickel. The same pipets were always used and they were rinsed out with the solution before the aliquot was taken. One of the cups was marked and it always contained the standard nickel solution, which occupied the left side of the colorimeter. After adding the reagent, the solutions were stirred with separate glass rods. These were bent into a triangle at the end to give more efficient stirring. The solutions were compared immediately.

A measurement required from ten to fifteen minutes. The temperature of the dark room was approximately 25°. The number of readings on the colorimeter for each solution was at least six. These were alternated, one being made as the height of the adjustable column of liquid was increased and the next as the height of the column was decreased. The total number of readings depended on how well they checked, more being taken if they did not agree closely. Usually eight or ten readings were made and the average taken.

To facilitate calculations the "unknown" solutions were set at some easily divisible number as 10, 20 or 30, and the standard adjusted to match this. The calculation was simply

$$\frac{\text{Reading of standard}}{\text{Setting of unknown}} \times \text{concn. of standard} = \text{mg. of nickel per ml. of unknown.}$$

Beer's Law.—Beer's law may be stated as follows. When equal heights or thicknesses of two solutions give the same intensity of color, the concentrations are equal. When equal color intensity is obtained from different heights of two solutions, the concentrations are inversely proportional to the heights, in accordance with Beer's law. This relationship forms the basis for colorimetry. In order for it to hold, the color formation in the two solutions must be perfectly formed, or imperfectly formed to the same extent in both solutions. It is sometimes the case in colorimetric analysis that the color formation is incomplete or unstable. This must be overcome by a calibration or correction curve which can be prepared experimentally from solutions of known concentrations.

The stock solution was used to make nickel solutions of various concentrations. The nickel solution to be diluted and the distilled water used were at 20 ± 1°. The concentrations varied from 0.1 to 0.001 mg. of nickel per ml. Ten ml. of each solution was compared with ten ml. of standard nickel solution as explained above. The amount of potassium dithio-oxalate added to each was sufficient for complete color reaction, because each set of measurements was duplicated with a larger amount of reagent.

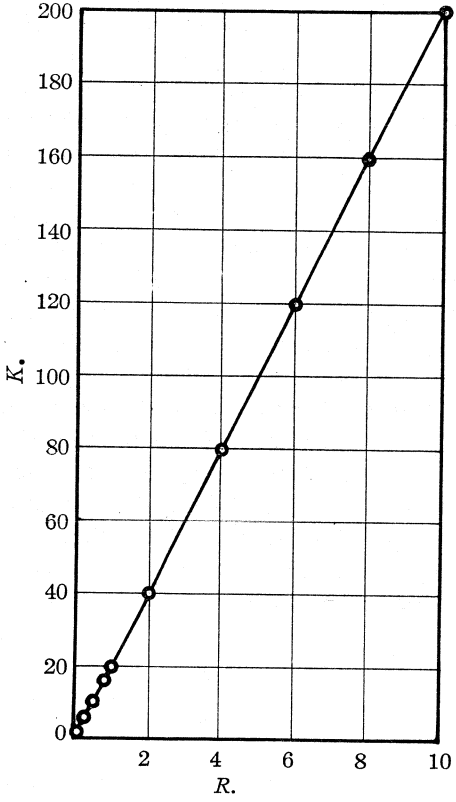


Fig. 1.

According to Beer's law a straight line is obtained by plotting the readings of the standards when the unknown solutions are set at 20.0, against the ratios of the height of standard over the height of unknown. Our results are shown graphically in Fig. 1. It is obvious that Beer's law is valid over the range in concentration studied and hence a correction curve is not required.

Sensitivity.—It is well known that in making color comparisons good results are not obtained with too deeply colored solutions. In practice, dilute solutions are either specified or implied. Horn[4] pointed out that the sensitiveness of solutions is a variable and that the ease of determination varies with the concentration. In general, it is believed that there is some one concentration at which a change in the intensity of the color can be more readily detected by the eye than at other concentrations. This concentration is in the range of dilute solutions. The *sensitivity* may be defined as *the reciprocal of the weight in milligrams of the constituent being determined that produces a change in color which can just be differentiated with certainty.*

Comparisons were made in a regular Nessler tube rack having a piece of black cardboard pasted on each side to shield the tubes from light. The solutions were made uniform by stirring. The colored solutions were measured from labeled pipets having 15, 10, 5, 3, 2 and 1 ml. capacity,

[4] Horn, *Am. Chem. J.*, **35**, 253–9 (1906).

respectively. For smaller quantities a 2-ml. pipet graduated to 0.1 ml. was used. The comparisons were made in daylight reflected from a white porcelain surface placed below the Nessler tubes and at a 45° angle. The comparisons were made at any hour of the day that was convenient and in cloudy as well as clear weather.

The standard colored solution was made from 10 ml. of the nickel standard and 1.6 ml. of a 0.1% potassium dithio-oxalate solution. It was usually made up in 100 ml. amounts. Portions of the standard colored solution were pipetted into Nessler tubes, each differing by a constant amount. These were then made up to 50 ml. with distilled water from a buret, and stirred thoroughly with a glass rod. The Nessler tubes were corked to prevent contamination. Different symbols and numbers were used so as not to indicate the arrangement to the observer. To avoid fading, comparisons were always made within two hours after the solution was prepared. Each series of tubes was compared and arranged in order of depth of color by five (occasionally four) observers. At another time these same concentrations, but freshly prepared solutions were arranged. This was repeated if the results were not in agreement with the first ones. In all cases the solutions were made and arranged out of order by one of us (F. H. W.) who was not making the comparisons.

The procedure followed was to pipet portions of the standard colored solution into the Nessler tubes, starting with zero ml. and increasing each by one ml. up to 12. These were always arranged in correct order. Then with a fresh solution, tubes were made each differing by the increment of half a ml. of colored solution. These were arranged in perfect order until the 10 ml. concentration was reached, when one observer could not tell the difference between the two tubes containing 10.0 and 10.5 ml., respectively. At this concentration, 0.5 ml. was the increment of colored solution which produced a change in color that could just be differentiated with certainty. Less labor was involved by working from one concentration, as 3 ml. of

TABLE I

MEASUREMENTS AND CALCULATED RESULTS

1 V	2 B	3 Δ	4 S	5 B'	6 Δ/B'	7 B/B'	8 $\sqrt{V}$	9 $\sqrt{S}$
34,930	0.0840	0.00420	238	0.08820	0.0476	0.953	187	15.42
43,675	.0672	.00336	297	.07056	.0476	.953	209	17.23
58,210	.0504	.00252	396	.05292	.0476	.952	241	19.90
87,320	.0336	.00168	595	.03528	.0476	.952	295	24.39
116,400	.0252	.000840	1190	.02604	.0322	.967	341	34.50
298,200	.00984	.000492	2032	.01033	.0476	.952	546	45.06
372,700	.00787	.000394	2538	.008266	.0476	.953	610	50.37
497,800	.00590	.000295	3390	.006198	.0476	.953	705	58.22
475,400	.00394	.000197	5075	.004133	.0476	.954	863	71.23
1,490,000	.00197	.000197	5075	.002165	.0909	.929	1220	71.23
9,314,000	.00033	Matched solution to which no nickel had been added.						

colored solution and 47 ml. of water. Other solutions were made up containing 2.8, 2.9, 3.0, 3.1 and 3.2 ml., respectively. In arranging these, no tube was out of order by more than one place. At this concentration, the amount which produces a perceptible difference is 0.1 ml. Solutions differing by less than a tenth of a ml. were not attempted. In weaker concentrations, say two ml. of colored solution, tubes having 1.8, 1.9, 2.0, 2.1 and 2.2 ml. were always arranged in correct order. Hence a standard nickel solution containing 0.001 mg. per ml. was used for smaller concentrations. This procedure was repeated for a number of concentrations. The measurements and their calculated results are recorded in Table I.

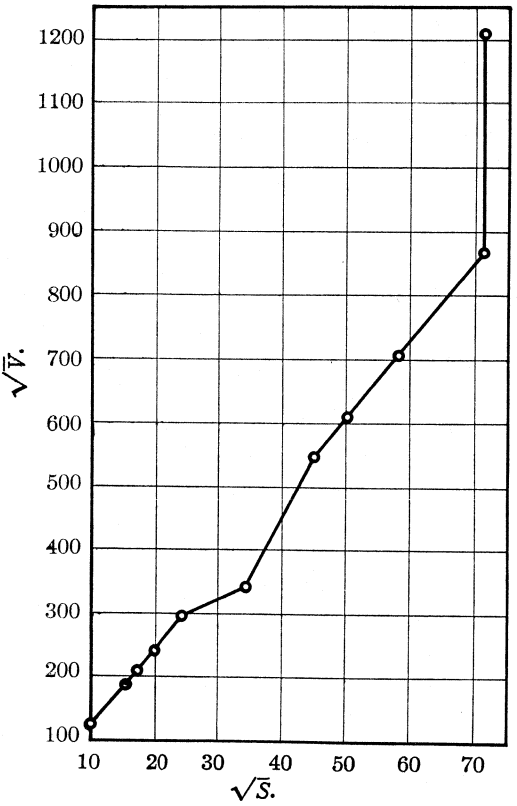


Fig. 2.

Column 1 gives the volume in liters containing one gram atom of nickel. In the second column B is the total milligrams of nickel in 50 ml. of solution. In column 3 Δ is the mg. of nickel producing a perceptible difference in the color intensity of 50 ml. of solution. $S = 1/\Delta$ = Sensitivity. $B' = B + \Delta$.

Figure 2 shows how the sensitivity varies with the concentration. In plotting the curve the square roots of the volume and of the sensitivity are used to make the graph less extensive. The sensitivity curve obtained for nickel is very similar to those obtained for other metals. Horn and Blake[5] made sensitivity curves for Cu^{++} and $CrO_4^{=}$ ions. Yoe and Hill[6] obtained sensitivity curves for aluminum by both the Aluminon and Alizarin Red S methods. The sensitivity of the Cu^{++} and $CrO_4^{=}$ ions increases greatly at a definite concentration, as shown in the curves of Horn and Blake. This is not true in the case of aluminum or nickel. Except for a slight break (maximum sensitivity range) in the curve for nickel and at

[5] Horn and Blake, *Am. Chem. J.*, **36**, 195–208 (1906).

[6] Yoe and Hill, THIS JOURNAL, **49**, 2395–2408 (1927); **50**, 748–756 (1928).

very dilute solutions, the sensitivity is a straight line function of the concentration. The setting of the standard nickel solution should be made at a point on the colorimeter scale which is within the range of maximum sensitivity.

The data in columns 6 and 7 show that over a wide range in concentration the ratios Δ/B' and B/B' are approximately constant. These ratios are also constant in the work of Horn and Blake and of Yoe and Hill. Δ/B' is the ratio between the amount of nickel which just suffices to produce a distinguishable difference in color, and the total amount of nickel present in 50 ml. of solution. This ratio is a constant except in too dilute solutions and where there is a break in the sensitivity curve. Horn and Blake[5] have shown that this value multiplied by 100 gives directly the percentage error inherent in the comparison of colors. Other sensitivity data show that the colored solutions may be too dilute, as well as too concentrated, to give the best results.

That the ratio Δ/B' is a constant follows from Weber's[7] psycho-physical law which states that a sensation is proportional to the natural logarithm of the stimulus, or that the increase of a stimulus necessary to cause an increase in sensation is a constant fraction of the whole stimulus. It is reasonable to assume that the stimulus is proportional to the amount of colored solute (or nickel) present. By definition, the sensitivity of the eye is a small increase in the sensation. From a mathematical consideration, Weber's law becomes

	Sensation	$= k \ln \text{stimulus}$	
Differentiating	d Sensation	$= k \, \text{d} \ln \text{stimulus}$	(1)
From Weber's law	Sensitivity of eye	$= \text{d sensation} = \text{constant} = k_1$	(2)
Assumption	Stimulus	$= k'$ concentration	(3)
Substituting (2) and (3) in (1)	Sensitivity of eye $= k_1$	$= k \, \text{d} \ln k' \text{ concentration}$	
		$= K \, \text{d} \ln \text{concentration}$	
Since d concentration $= \Delta$		$= \dfrac{K\Delta}{\text{concentration}}$	(4)

Equation 4 is the statement of Fig. 2, namely, that the sensitivity, that is, $1/\Delta$, varies inversely as the concentration. Hence it follows that the ratio Δ/B' is a constant fraction of the total weight of nickel present.

B/B' is also constant and is the ratio between the total amounts of nickel in two 50-ml. tubes containing colored solutions that can just be distinguished with certainty. Horn and Blake[8] obtained for this ratio the average values of 0.92 and 0.95 for Cu^{++} ions and $[Cu(NH_3)_4]^{++}$ ions, respectively. They suggest the possibility that B/B' is a constant, independent of the color examined. This seems to be approximately true as indicated by all the known sensitivity work compiled in Table II.

[7] Hackh, "A Chemical Dictionary," P. Blakiston's Son and Co., Philadelphia, 1929.

[8] Horn and Blake, *Am. Chem. J.*, **36**, 516–22 (1906).

TABLE II

Ion	Method	Color	B/B', av. values	Observer
Al^{+++}	Aluminon	Red	0.92	Yoe and Hill
Al^{+++}	Alizarin	Red	.89	Yoe and Hill
CrO_4^-	CrO_4^-	Yellow	.96	Horn
Cu^{++}	Cu^{++}	Blue	.92	Horn and Blake
Cu^{++}	$[Cu(NH_3)_4]^{++}$	Dark blue	.95	Horn and Blake
Ni^{++}	$K_2NiC_4O_4S_4$	Magenta	.95	Yoe and Wirsing

In calculating B/B', values were omitted at each end of a series of measurements where the percentage error inherent in the comparison was large. This constant tends to become unity and its average value is usually above 0.90. In a series of measurements with solutions of any colored ion or molecule, the ratio B/B' approaches unity at the highest sensitivity. It is noted in the case of aluminum, using two different methods, but both giving approximately the same color, that the one with the higher average value of B/B' is the more sensitive.

The potassium dithio-oxalate–nickel reaction is very sensitive. Jones and Tasker[1] detected nickel at a dilution of one part in 40 million parts of solution, when the solution filled a beaker, and one part in 8 millions using a test-tube. Our experiments show that 0.008 mg. of nickel can be detected in a liter of solution, *i. e.*, one part of nickel in 125 million parts of solution, when the observation is made in a 50-ml. (210-mm.) Nessler tube.

Optimum Experimental Conditions

In order to find the optimum experimental conditions, the effect of both the volume and the concentration of the reagent was determined. Ten ml. of standard nickel solution was compared with ten ml. of a nickel solution containing 0.008 mg. per ml. The reagent for the latter solution was added in small amounts and a comparison made after each addition until the intensity remained constant. The amount of reagent just sufficient for complete color formation was 1.2 ml. of a 0.05% $K_2C_2O_2S_2$ solution. This was repeated using a 0.1% reagent solution and 0.6 ml. was required. The weight of $K_2C_2O_2S_2$ was the same in both cases, but the volumes were different. Because of this unequal dilution of the nickel solution by the reagent, sufficient distilled water was added to the smaller volume to make the total volume of each the same.

A large excess of reagent causes a different shade or tint of color to develop, which is lighter than the red color of the potassium nickelo-dithio-oxalate. This fading appears more quickly for a large excess of reagent than for a small excess. Table III shows how quickly the fading appears when an excess of 0.1% reagent is used with 10 ml. of standard nickel solution.

TABLE III

Excess reagent, ml.	1.5	1.0	0.5	0.0
Time before fading, min.	15	30	75	300

With no excess reagent, fading is not very marked until the end of two days. However, with this concentration fading was never noticed under five hours and satisfactory readings have been made after twelve hours. The order of addition of reagents and nickel appears to make no difference, although it was always the same in this work.

Jones and Tasker represent the reaction of potassium dithio-oxalate with nickel salts by the equation: $2\,K_2C_2O_2S_2 + NiX_2 = K_2(C_2O_2S_2)_2Ni + 2\,KX$. The colored compound is potassium nickelo-dithio-oxalate, as shown by several analyses.

	Per cent. by analysis	Per cent. for $K_2NiC_4O_4S_4$
C	12.78	12.74
S	34.4	34.0
Ni	16.2	15.8

The theoretical amount of reagent required for a definite amount of nickel may be calculated from the above equation, and is 0.0675 mg. of $K_2C_2O_2S_2$ for 0.01 mg. of nickel. The amount of $K_2C_2O_2S_2$ experimentally required for 0.01 mg. of nickel was 0.080 mg. A solution of known nickel content was compared with the nickel standard. The reagent solution was added in small increments, a comparison being made after each addition. When the average reading on the colorimeter indicated the correct amount of nickel for the known solution, an excess of reagent never increased the intensity of the color. This procedure was repeated on a series of solutions of known nickel content.

The heavy line in Fig. 3 shows the amount of potassium dithio-oxalate required for various amounts of nickel as determined experimentally. The theoretical amount of reagent is shown by the

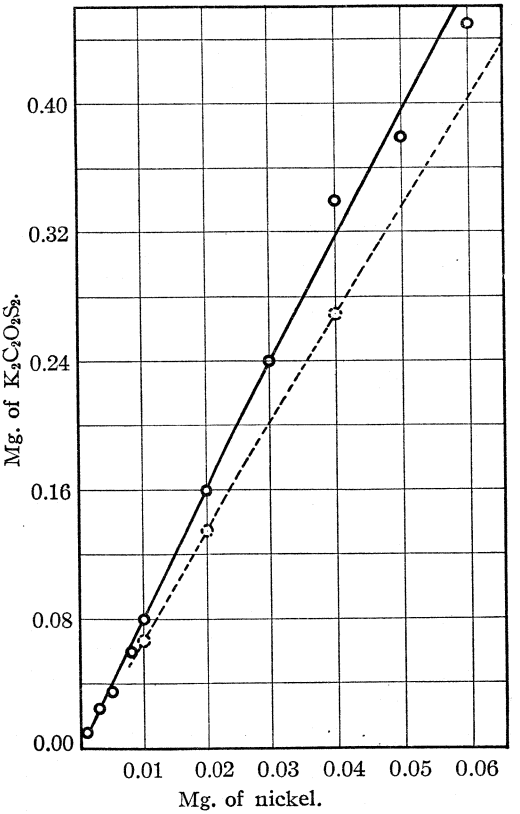


Fig. 3.

broken line. It is evident that all of the reagent is not reacting with the nickel. This is due to a slight decomposition of the reagent.

The instability of the potassium dithio-oxalate was the most troublesome factor in this investigation. The salt was light straw colored when obtained but gradually changed to brown. Dilute solutions are colorless; concentrated ones are yellow. Jones and Tasker reported that evaporation of the reagent solution on the water-bath gives a deposit of large colorless prisms. The salt is white when recrystallized from alcohol, but on recrystallizing from water it becomes less stable. On keeping, it turns brown. The brown coloration does not seem to be due to the presence of sulfide or free sulfur. Under the microscope particles of different color are visible, but these are very soluble in water.

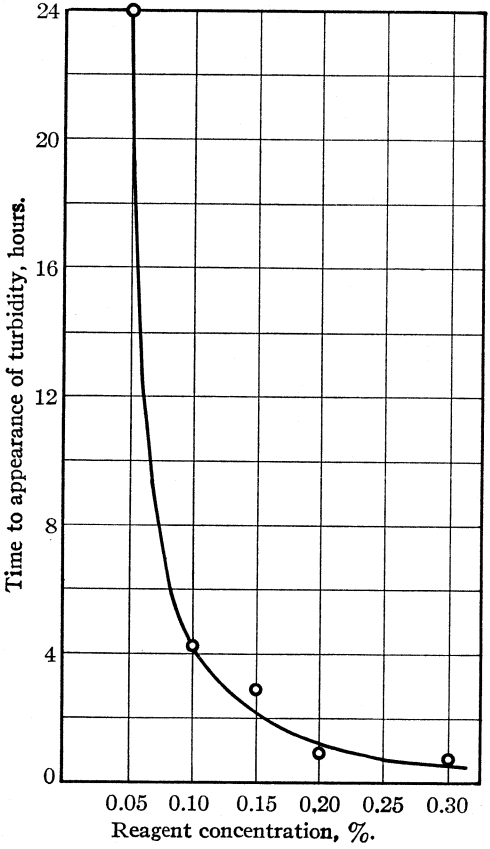


Fig. 4.

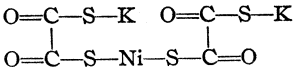
After a reagent solution has stood for some time, there forms a yellow turbidity which gradually settles out as a yellow precipitate. In the first part of our work measurements indicated that this did not appear so soon if the oxygen dissolved in the distilled water was boiled out before making the reagent up to volume. It so happened that measurements with ordinary distilled water were carried out in the direct sunlight, while those with "oxygen-free" distilled water were not. Later measurements showed that sunlight produces cloudiness more readily than the oxygen in the water. For example, a 0.3% reagent solution made up with "oxygen-free" water showed no noticeable cloudiness in fifty minutes. The same strength reagent made with ordinary distilled water and allowed to stand under the same conditions became noticeably turbid in forty minutes. However, a portion of this same solution kept in the dark room was not cloudy in three days.

The curve in Fig. 4 shows the rate of appearance of turbidity in po-

tassium dithio-oxalate solutions at concentrations ranging from 0.05 to 0.30%. It is obvious that a 0.05% reagent solution is preferable to one more concentrated.

The stability of potassium dithio-oxalate in solution is affected by the hydrogen-ion concentration. An excess of hydrogen ions decomposes the reagent, while an excess of hydroxyl ions prevents it from becoming cloudy. For example, a 0.1% reagent solution in 0.002 *N* potassium hydroxide developed no turbidity upon long standing. In lower concentrations of alkali, turbidity appears more slowly than in neutral solution. Higher alkali concentrations cause the reagent solution gradually to turn yellow on standing for several weeks. Portions of a 0.1% reagent solution made acid with varying amounts of 0.1 *N* sulfuric acid all gave precipitates, the amount increasing with increase in acidity.

Potassium nickelo-dithio-oxalate is relatively stable. Upon standing in solution for several weeks it loses its red color, but no cloudiness or precipitation appears. Its structural formula may be written as



The effect of acidity or alkalinity on the colored potassium nickelo-dithio-oxalate solutions was observed by mixing 10-ml. portions of standard nickel solution with the required quantity of reagent and then adding varying amounts of acid or alkali. Alkali causes a fading of the colored solution. Even as small an amount as 0.2 ml. of 0.0174 *N* potassium hydroxide was sufficient to give incorrect colorimeter readings with 10 ml. of the standard nickel solution. Varying amounts of acid up to 0.8 ml. of 0.0194 *N* sulfuric acid in 10 ml. of standard nickel solution did not seriously affect the colorimeter readings but larger amounts gave a lighter shade of color than the characteristic pink. Hence, the final acidity of the colored nickel solution should not be over 0.002 *N* in sulfuric acid.

Effect of Various Ions.—Many metallic ions react with potassium dithio-oxalate to form colored compounds. Jones and Tasker observed color reactions with the following: Sb, Bi^{+++}, Cd^{++}, Co, Cu^{++}, Fe^{++}, Fe^{+++}, Mn, Hg^{+}, Hg^{++}, Ag^{+}, Sn^{++}, Sn^{++++}, Pd, Pt^{++}, Zn^{++}, Ce^{++++}, Au, Tl, Ti^{+++} and V. It is evident that any of the above ions may interfere with the nickel determination. Ions that give no color reaction are Al^{+++}, Ca^{++}, Ba^{++}, Sr^{++} and Mg^{++}. Iron and cobalt ions are the ones most likely to interfere with the nickel determination. Their concentration must be under one-hundredth that of the nickel; otherwise, an appreciable error results.

Summary

A study of the reaction between potassium dithio-oxalate and nickel has been made with reference to its use in colorimetry. The reaction obeys

Beer's law over a range in concentration suitable for colorimetric analysis. The sensitivity, optimum experimental conditions and the effect of various ions have been determined. Best results were obtained with a 0.05% reagent solution and a nickel concentration of ten mg. per liter. The reagent will detect one part of nickel in 125 million parts of solution, when the observation is made in a 50-ml. (210-mm.) Nessler tube. The color develops satisfactorily in sulfuric acid solution up to approximately 0.002 normal. Traces of alkali cause fading. Many metallic ions give color reactions with the reagent and hence will interfere with the nickel determination unless they are removed. Iron and cobalt are the ions most likely to interfere and must be removed unless the nickel concentration is at least a hundred times greater than that of these ions.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE HOMOGENEOUS COMBINATION OF ETHYLENE AND HYDROGEN. A SECOND-ORDER ASSOCIATION REACTION

BY ROBERT N. PEASE

RECEIVED JANUARY 4, 1932 PUBLISHED MAY 7, 1932

It has recently been shown that the polymerization of ethylene at pressures above one atmosphere is a second-order homogeneous gas reaction.[1] The primary action is thus of the association type. In view of the fact that many homogeneous dissociation reactions are known to be first order, it was inevitable that second-order homogeneous association reactions should occur, unless the classical principle of mobile equilibrium is incorrect as ordinarily applied. Nevertheless, a theoretical difficulty has arisen in this connection which makes it especially desirable to investigate other cases. The hydrogenation of ethylene is a particularly suitable example since the reaction is reversible,[2] and the reverse action (dissociation of ethane) has been rather definitely shown to be first order.[3]

The theoretical difficulty mentioned above has to do with the accommodation of energy in a single product molecule newly formed by the collision of two reactant molecules. A rather crude analogy on a large scale is the cohesion of two "sticky" masses—say, two balls of tar—which have been directed at each other. In the latter case, any kinetic energy which is lost, and the cohesion energy are converted into internal energy of the resulting mass. Similarly in the case of two associating molecules, the

[1] Pease, THIS JOURNAL, **53**, 613 (1931). At lower pressures there is evidence of deviation. See Pease, *ibid.*, **52**, 1158 (1930). The polymerization of acetylene may also be second order. See Pease, *ibid.*, **51**, 3470 (1929).

[2] Pease and Durgan, *ibid.*, **50**, 2715 (1928).

[3] Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931); Frey and Smith, *ibid.*, **20**, 948 (1928).

product molecule is called upon to accommodate in internal degrees of freedom any loss of kinetic energy due to the inelastic nature of the collision, plus the reaction energy, and the internal energies of the original molecules. However, since internal degrees of freedom are in general quantized, the chance that the product molecule should be able to do this appears to be negligible. The association is, therefore, extremely improbable.

The solution of this apparent difficulty was suggested by Kassel.[4] The above argument implies that the internal degrees of freedom must be quantized *immediately* the molecule is formed. This cannot be assumed. Rather, the uncertainty principle indicates that the energies of individual states may differ from their final values by as much as $h/\Delta t$, where Δt is the time from the instant of collision. Therefore, if the total energy levels are spaced sufficiently closely, any value of the energy may be temporarily accommodated by the product molecule. Eventually, of course, any excess of energy over that exactly corresponding to some particular set of energy levels must be converted into kinetic energy in another collision, if the product molecule is to be stabilized.

The simplest reaction mechanism appears to be essentially that suggested by Taylor for the ethylene polymerization.[5] Two molecules whose joint energy exceeds some minimum may unite on collision. The resulting quasimolecule may subsequently either dissociate spontaneously, or it may be dissociated as a result of a collision, or, finally, it may be stabilized as a result of a collision. Which of the last two happens will depend on the state of the molecule at the instant of collision. The rate of association will be

$$\alpha Z_0 e^{-E/RT} c_1 c_2$$

where α is an orientation factor, Z is the total collision rate at unit concentrations and E is the activation energy. If most quasi-molecules of products survive to undergo a collision (instead of decomposing spontaneously), the observed reaction rate will then be given by

$$\alpha\beta z_0 e^{-E/RT} c_1 c_2$$

where β is the fraction of subsequent collisions in which the quasi-molecule is stabilized, rather than decomposed. In the case of ethylene polymerization the product $\alpha\beta$ was found to be about 1/2000. As will be shown later, it is more nearly unity for the hydrogenation of ethylene.

Apparatus and Method

The apparatus and method were standard. The reaction was followed by measuring the pressure decrease at constant volume in a heated Pyrex reaction vessel of 500 cc. volume. After a measurement was completed, the reaction mixture was collected with a Töpler pump and analyzed.

[4] Kassel, THIS JOURNAL, **53**, 2143 (1931).

[5] Pease, *ibid.*, **53**, 613 (1931).

The hydrogen was purified by passage over hot platinized asbestos, and through a trap at −79°. The ethylene was purified by fractionation. Both gases were originally better than 99% pure.

Results

The experiments were subject to two limitations. Owing to simultaneous polymerization of ethylene, it was necessary to confine the measurements to mixtures containing a 3:1 excess of hydrogen. Satisfactory results were then obtained when the reaction vessel was unpacked. When, however, the vessel was filled with broken glass, it was found that considerable quantities of hydrogen were absorbed by the latter.[6] As a result, the observed pressure decrease (at 550°) was about twice that with the empty vessel. Analysis of the gas reaction mixture after exposure showed clearly that the rate of ethane formation was normal. This is the more interesting since it shows that the absorbed hydrogen is not reactive.

The values of k_2 were calculated by means of the equation

$$k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

where t is the time in seconds, a is the initial pressure of hydrogen, b is the initial pressure of ethylene and x is the pressure of ethane at time t. In calculating values of k_2, the first measurement ($t = 300$) was taken as the initial state.

Since the reaction is reversible, it was necessary to determine whether the reverse action was interfering to an appreciable extent. It was found that the values of k_2 were not appreciably different when the much more elaborate expression involving the rate of the reverse action was employed. Measurements were only carried up to 50% conversion of the ethylene.

The results of a series of experiments with $3H_2$:$1C_2H_4$ mixtures carried out in the unpacked reaction vessel are presented in Table I. It will be seen that the values of k_2 are reasonably constant at each temperature. At 550° measurements were made with initial total pressures of one, one-half and one-fourth atmosphere. Although the constants at one-half atmosphere were somewhat lower than the others, there is no reason to doubt that the reaction is second-order.

It has already been mentioned that polymerization of ethylene interfered when the reaction mixture contained more than 25% of this gas. This is shown by the data of Table II. Two runs were made at 550° with mixtures of $2H_2$:$1C_2H_4$ and $1H_2$:$1C_2H_4$. In each case the amount of hydrogen reacting was nearly the same as the amount of ethane formed. The amount of ethylene reacting exceeded this latter by 11% with the $2H_2$:-$1C_2H_4$ mixture, and by 33% in the $1H_2$:$1C_2H_4$ mixture. In consequence it is not possible to calculate a constant for the formation of ethane. Ap-

[6] Compare Alyea, THIS JOURNAL, 53, 1324 (1931).

TABLE I

RATES WITH $3H_2:1C_2H_4$ MIXTURES IN EMPTY REACTION TUBE

Temp., °C.	475		500		524		552		548		550	
Initial press. H_2, mm.	573		575		580		562		294		141	
Initial press. C_2H_4, mm.	195		196		198		191		100		48	
Initial total press., mm.	768		771		778		753		394		189	
Time, sec.	Obs. press.	$k_2\times10^7$	Obs. press.	$k_2\times10^7$	Obs. press.	$k_2\times10^7$	Obs. press.	$k_2\times10^7$	Obs. press.	$k_2\times10^7$	Obs. press.	$k_2\times10^7$
300	762		756		747		717		380		183	
600	758	(1.3)	749	2.43	733	5.39	685	15.1	371	13.4	180	(19)
900	755	(1.1)	743	2.25	720	5.50	661	15.1	363	13.6	178	16
1200	752	1.08	737	2.24	709	5.42	Av.	15.1	356	13.6	176	15
1800	747	0.99	725	2.31	690	5.37			345	13.4	172	16
2700	739	0.98	708	2.40	667	5.40			Av.	13.5	168	15
3600	732	0.95	693	2.47	Av.	5.42					Av.	16
4500	723	1.01	680	2.51								
7200	703	1.01	Av.	2.37								
	Av.	1.00										
Final press. change, mm.	65		91		111		92		49		21	
C_2H_6 formed, mm.	64		92		119		108		58		28	
C_2H_4 used, mm.	60		87		107		89		47		24	
H_2 used, mm.	69		96		124		112		62		25	

TABLE II

REACTION AT 550° WITH $2H_2:1C_2H_4$ AND $1H_2:1C_2H_4$ MIXTURES

Temp., °C.	548	550
Initial % C_2H_4	33.1	49.2
Initial total press., mm.	768	766
Final total press., mm.	620	565
Pressure drop, mm.	148	201
C_2H_6 formed, mm.	141	184
H_2 reacted, mm.	146	187
C_2H_4 reacted, mm.	157	245
CH_4 formed, mm.	10	35
Higher unsats. formed, mm.	4	12
Reaction time, sec.	1800	2700
$k_2 \times 10^7$	(11.4)	(10.7)

proximate calculations indicate that the value of k_2 may be somewhat less in these mixtures. Thus, the most favorable view that could be taken would be that the whole pressure drop is due to ethane formation. The corresponding calculation of k_2 gives 11.4×10^{-7} for the $2H_2:1C_2H_4$ mixture, and 10.7×10^{-7} for the $1H_2:1C_2H_4$ mixture, as compared with 15.1×10^{-7} for the $3H_2:1C_2H_4$ mixture.

Experiments with the reaction vessel filled with broken Pyrex glass (4–10 mesh) are recorded in Table III. Analysis showed that in all cases there was a marked loss of hydrogen in excess of ethane formed. In this case also it is not possible to give precise values of k_2. Assuming that the whole pressure drop represents reaction, the values of k_2 would be 4.15×10^{-7} at 500° and 1 atm. (initial), and 27.4×10^{-7} at 550° and 1 atm. (initial). These are to be compared with 2.37×10^{-7}, and $15\ 1 \times 10^{-7}$, respectively,

in the empty tube. The constants for the packed tube are nearly twice those for the empty tube. Even if this were all due to increased wall reaction in the packed tube, it would still not be serious since the wall surface has been increased by a factor of ten at least. However, the results of analysis show clearly that twice as much hydrogen as ethylene has disappeared, which accounts for the large apparent value of k_2. In the experiment at 550° the final reaction mixture was fractionated before analysis. The result proved that ethane, rather than a mixture of methane and propane (say), was produced.

TABLE III

REACTION OF $3H_2$:$1C_2H_4$ MIXTURE IN PACKED REACTION VESSEL

Temp., °C.	499	550	550
Initial press. H_2, mm.	564	563	335
Initial press. C_2H_4, mm.	193	193	115
Initial total press., mm.	757	756	450
Final total press., mm.	694	648	390
Pressure drop, mm.	63	108	60
C_2H_6 formed, mm.	45	83	39
H_2 reacted, mm.	72	126	68
C_2H_4 reacted, mm.	38	65	31
Reaction time, sec.	1800	600	900
$k \times 10^7$	(4.15)	(27.4)	(27.3)

Discussion

The results show that the formation of ethane from ethylene and hydrogen is a homogeneous, second-order reaction, at least when hydrogen is in excess. It remains to calculate the reaction rate on the basis of the collision theory.

The values of k_2 for the runs at one atmosphere in the empty bulb with a $3H_2$:$1C_2H_4$ mixture are fitted by the equation

$$\log_{10} k_2 = -\frac{43{,}150}{2.303RT} + 5.576$$

as shown by the data of Table IV.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED VALUES OF k_2

Temp., Å.	$k_2 \times 10^7$ Obs.	Calcd.
748	1.00	0.97
773	2.37	2.45
797	5.42	5.70
825	15.1	14.5

According to the collision theory, the rate of reaction in terms of molecules of ethane formed per cc. per second should be

$$\alpha\beta 2\sqrt{\frac{2\pi RT(M_1 + M_2)}{M_1M_2}}\,\sigma_{12}^2 n_1 n_2 e^{-43{,}150/RT}$$

where M_1 is the molecular weight of H_2, M_2 is the molecular weight of C_2H_4, σ_{12} is the average diameter of H_2 and C_2H_4 in cm., n_1 is the number of mols. of H_2 per cc. and n_2 is the number of mols. of C_2H_4 per cc. α and β have been already defined. Since σ_{12} can only be approximately estimated in the absence of viscosity determinations at the temperatures of the experiments, it seems best to use the velocity data to calculate $\alpha\beta\sigma_{12}^2$. An estimate of $\alpha\beta$ can then be made by substituting a reasonable value of σ_{12}.

k_2 represents the pressure in mm. of C_2H_6 formed per second when C_2H_4 and H_2 are at 1 mm. pressure each. At 500° (773 Å.) k_2 is 2.45×10^{-7}. This corresponds to 3.08×10^9 molecules of C_2H_6 formed per cc. per second. At 550° and 1 mm. pressure there will be 1.25×10^{16} molecules each of H_2 and C_2H_4 per cc. Substituting

$$\frac{3.08 \times 10^9}{(1.257 \times 10^{16})^2} = \alpha\beta\sigma_{12}^2 . 2\sqrt{\frac{2\pi 8.32 \times 10^7 \times 773 \times 28.0}{24.0 \times 4.03}} . e^{-\frac{43{,}150}{1.985 \times 773}}$$

$$\alpha\beta\sigma_{12}^2 = 4.38 \times 10^{-17}$$

If now we assume that

$$\sigma_{H_2} = 1 \times 10^{-8}$$
$$\sigma_{C_2H_4} = 4 \times 10^{-8}$$

then

$$\sigma_{12}^2 = 4 \times 10^{-16}$$

whence $\alpha\beta = 0.1$, approximately. Thus, of all collisions between H_2 and C_2H_4 molecules having the requisite energy, about 10% lead to formation of C_2H_6. This is to be compared with 0.05% (1/2000) in the combination of ethylene molecules.

Comparison with Equilibrium Data and Rate of Dissociation of Ethane.—If the velocity constant for the combination of ethylene and hydrogen is k_2, and the constant for dissociation of ethane is k_1, the equilibrium constant for the dissociation of ethane

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

is given by

$$K = \frac{p_{C_2H_4} p_{H_2}}{p_{C_2H_6}} = \frac{k_1}{k_2}$$

The experiments here reported give for k_2 in mm.

$$\log_{10} k_2 = -\frac{43{,}150}{2.3RT} + 5.576$$

For k_2 in atmospheres, this becomes

$$\log_{10} k_2 = -\frac{43{,}150}{2.3RT} + 8.457$$

For k_1, the work of Marek and McCluer[3] gives

$$\log_{10} k_1 = -\frac{73{,}170}{2.3RT} + 15.12$$

Thus

$$\log_{10} K = \log_{10} k_1 - \log_{10} k_2 = -\frac{30{,}020}{2.3RT} + 6.66$$

Direct measurements of K at 600–700° give[2]

$$\log_{10} K = -\frac{31{,}244}{2.3RT} + 6.31$$

The independent determinations thus confirm one another.

Summary

The combination of ethylene and hydrogen in a Pyrex glass vessel at 475–550° and one atmosphere pressure has been shown to be a homogeneous, second-order reaction. A calculation based on the collision theory indicates that about 10% of the collisions between ethylene and hydrogen molecules possessing the requisite energy (43,150 cal. per mole) eventually result in formation of ethane.

Combination of equations for the rates of ethane formation and of ethane dissociation gives an equation for the equilibrium constant of the reaction

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

in good agreement with that obtained by direct measurement.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

THE PREPARATION AND PROPERTIES OF IODINE MONOCHLORIDE[1]

BY JACOB CORNOG AND R. A. KARGES

RECEIVED JANUARY 4, 1932 PUBLISHED MAY 7, 1932

I. Preparation

Old Method.—Iodine monochloride has usually been prepared by leading chlorine over solid iodine.[2] The crude product thus obtained was distilled; the portion of the distillate forming between 100 and 102° was retained. The distillate was far from pure. Stortenbecker[3] obtained iodine monochloride of good quality by repeatedly recrystallizing the distillate in its own mother liquor.

Improvement of the Old Method.—The present authors found that passing a slow stream of chlorine through the system during distillation and collecting the distillate formed between 100 and 101.5° increased the yield from about 35 to about 85% and also improved the quality of the

[1] From a thesis submitted to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy, by R. A. Karges, August, 1931.

[2] Gay-Lussac, *Ann. chim.*, **91**, 1 (1814); Serullas, *Ann. chim phys.*, **22**, 180 (1833); Harmay, *J. Chem. Soc.*, **26**, 815 (1873); *ibid.*, **35**, 269 (1879); Thorpe, *ibid.*, **37**, 174 (1880); **61**, 925 (1892).

[3] Stortenbecker, *Rec. trav. chim.*, **7**, 152 (1888).

distillate. They also found that analyzing the distillate and adding the quantity of solid iodine required to cause the compositions to correspond to that implied by the formula of iodine monochloride was a profitable expedient. The iodine monochloride was next liquefied and then slowly cooled, whereupon large, black, prism-shaped crystals formed. When about 80% of the iodine monochloride had crystallized, the remaining liquid was removed by decantation. This process was repeated until the freezing point of the crystals was the same as that of the supernatant liquid. Two or three crystallizations were usually required. At best this older method is a tedious, time-consuming process.

A New Method of Preparation.—The statement of Thomas and Dupuis[4] that solid iodine added to liquid chlorine leads to the formation of iodine trichloride suggested the method for preparing iodine monochloride about to be described. Approximately 300 ml. of liquid chlorine is led directly from a commercially obtained cylinder of chlorine into a tared 500-ml. flask cooled with a mixture of solid carbon dioxide and ether. A weighed quantity of solid iodine, roughly one-half of a molar equivalent of the chlorine in the flask, is next added. The equivalence may vary rather widely but the weight should be accurate. After the addition of iodine the contents of the flask congeal to a solid. The flask is gradually raised from the cooling mixture and allowed to warm to room temperature. During the warming any uncombined chlorine evaporates. The weight of the flask and contents is next determined. Since the weight of the iodine added and the tare weight of the flask are known, the weight of the chlorine is determined by difference. The weight of both chlorine and iodine being known, the quantity of solid iodine that must be added to cause the composition of the impure product to correspond to that implied by the formula ICl is computed and added. The flask is closed with a glass stopper and allowed to stand in a liquid condition for twenty-four hours or longer. The freezing point of the iodine monochloride is usually within 0.1° of that of the pure article. One or two recrystallizations usually suffice to obtain the pure iodine monochloride. The following manipulative observations are helpful. Iodine monochloride vigorously attacks cork, rubber and the human skin, hence contacts with these substances should be avoided. A dilute (6 *M*) solution of hydrochloric acid is an effective antidote for skin burns. While iodine monochloride in bulk is not notably hygroscopic, yet small quantities of moisture from the air or starting materials will noticeably depress the freezing point. Hence exposure to moisture should be at a minimum. Exposure to atmospheric moisture produces a film of iodine pentoxide on the glass of the containing vessel.

By this new method the authors have been able to prepare pure iodine

[4] Thomas and Dupuis, *Compt. rend.*, **143**, 282 (1906).

monochloride in one or two kilo lots within two or three hours. Preparation of similar quantities by the older methods required a similar number of days. This procedure serves also for the preparation of iodine trichloride but the authors have investigated this only qualitatively.

The iodine monochloride prepared as described had a freezing point of 27.19° as compared with the Stortenbecker value of 27.20°. The thermometer used was marked in 0.1° divisions and had been compared with a similar thermometer calibrated by the United States Bureau of Standards. A second criterion of purity was that afforded by gravimetric analysis. The method was a modification of the one described by Stortenbecker.[5] Duplicate analyses of the same sample would not vary by more than 0.2%, generally by not more than 0.1%, from each other and from the theoretical composition of iodine monochloride. A third criterion of purity was the similarity of values obtained for the electrical conductivity of iodine monochloride obtained in different runs.

The conjunction of the criteria led to the belief that the iodine monochloride used in these experiments was approximately pure.

II. Vapor Pressure

The vapor pressure was measured by the method of Smith and Menzies.[6] Iodine monochloride was the confining liquid. When heated above 70° the rate of decomposition of iodine monochloride becomes so rapid that consistent measurements were not obtained. The average of four experimentally determined vapor pressure values at each temperature is recorded in the third column of Table I. The individual measurements did not vary more than 0.25 mm.

TABLE I

VAPOR PRESSURE AND OTHER DATA CONCERNING IODINE MONOCHLORIDE

Temp., °C.	Absolute temp., °K.	Vapor pressure of ICl, mm.	ΔH, molal heat of vaporization, cal.	$\Delta H/T$, boiling entropy of vaporization, cal.
35	308.1	48.0		
40	313.1	62.5	10,140	27.18
45	318.1	81.0	10,290	27.59
50	323.1	103.6	10,080	27.02
55	328.1	131.9	10,200	27.34
60	333.1	166.0	10,100	27.08
65	338.1	209.0	10,302	27.66
70	343.1	261.7	10,460	28

The values for molar heat of vaporization given in column four were computed by the use of the integrated form of the Clausius–Clapeyron equation.

$$2.302 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \frac{T_2 - T_1}{T_2 T_1}$$

[5] Stortenbecker, *Z. physik. Chem.*, **10**, 192 (1892).

[6] Smith and Menzies, THIS JOURNAL, **32**, 1427 (1910).

P_2 and P_1 are vapor pressures at temperatures T_2 and T_1, respectively. ΔH is the molar heat of vaporization.

According to Trouton's rule, the entropy of vaporization for non-associated liquids is 21 calories.

Since iodine monochloride dissociates on boiling at atmospheric pressure, its boiling point is not definite. The literature gives values as low as 94.7 and as high as 102. The value used in the computation of column 4 is 100° or 373.1°K. The values given in column 5 indicate that iodine monochloride is an associated or polar liquid. J. H. Hildebrand[7] makes the point that, for the application of Trouton's rule, the entropy of vaporization should be taken, not when liquids are boiled under atmospheric pressure, but rather when temperature and pressure are so chosen as to give the same volume of vapor per mole of material in each case.

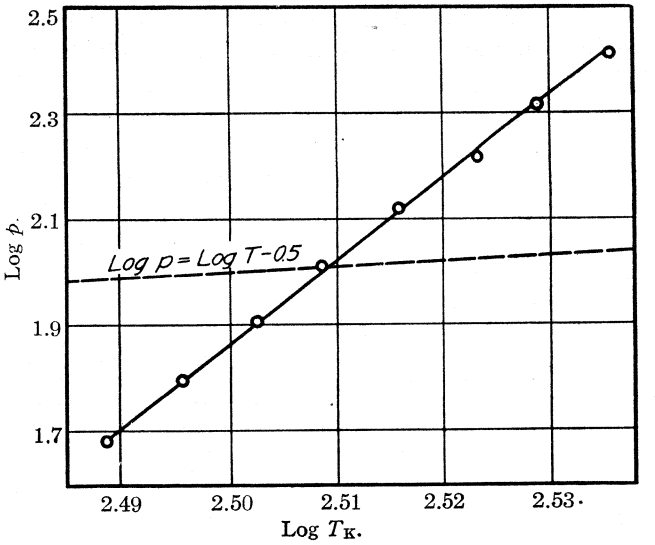


Fig. 1.

By applying a modification of the Clausius–Clapeyron equation to the data given graphically in Fig. 1, the value of the entropy of vaporization of iodine monochloride is computed as 33.4 cal. at the concentration of 0.00507 mole per liter. Hildebrand gives the values of this constant at this concentration as 32.4 cal. for liquid ammonia, 32 cal. for water and 33.4 cal. for ethyl alcohol. For ten known non-associated liquids he gives the average value of 27.4 cal. at this concentration.

Iodine monochloride is an associated or polar liquid.

[7] J. H. Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 93.

III. The Conductivity of Iodine Monochloride

An ordinary conductivity cell was used to measure the conductivity of iodine monochloride and of solutions of potassium chloride and ammonium chloride in it. The cell constant was obtained in the usual way by measuring the conductivity of a 0.02 *M* solution of potassium chloride in water. The measurements were made in a thermostat at 35 ± 0.1°. The specific conductivity of four different samples of iodine monochloride varied from 0.004572 to 0.004589 reciprocal ohms.

Prolonged exposure of iodine monochloride in a wide weighing bottle to the humid air of a June day caused the sides and bottom of the bottle to become heavily coated with iodine pentoxide. This exposure also influenced the conductivity of iodine monochloride. Removing the stopper of the conductivity cell for two minutes produced no measurable change in conductivity; exposure for twenty minutes in the weighing bottle caused the specific conductivity to increase from 0.004589 to 0.00521 and exposure for one hundred minutes increased the conductivity to 0.01327 reciprocal ohms.

The results of vapor pressure measurements indicate that iodine monochloride is an associated liquid; hence it may be expected to act as an ionizing solvent. The validity of this assumption may be put to experimental proof by preparing solutions of potassium chloride and of ammonium chloride and measuring the conductivity at different dilutions. The results are given in Table II.

TABLE II

CONDUCTIVITY OF SOLUTIONS IN IODINE MONOCHLORIDE AT 35°

Molal concn. of solute	Specific conductivity of cell	*K*, specific conductivity of solute	Equivalent conductivity
	Potassium chloride as solute		
0	4583×10^{-6}	...	...
0.5	18,975	$14,387 \times 10^{-6}$	28.76
.25	12,140	7,522	30.21
.125	8,494	3,996	31.20
.0625	6,491	1,903	30.43
.02083	3,230	642	30.81
.00993	4,797	84	31.19
	Ammonium chloride as solute		
0	4588	...	...
1	24,175	19,650	19.65
0.5	15,770	10,982	21.96
.33⅓	12,100	7,852	22.64
.16⅔	8,558	3,970	23.82
.08⅓	6,642	2,034	24.64

Columns one and four in Table II are graphically represented in Fig. 2. These data indicate that: (1) Potassium chloride dissolved in iodine mono-

chloride increases the conductivity very decidedly. However, after the first dilution the equivalent conductivity shows no regular increase with dilution. (2) Ammonium chloride also shows evidence of dissociation in the solution. While the equivalent conductivity is less than in water, its increase with dilution is entirely analogous to the behavior of a solution of an electrolyte in water.

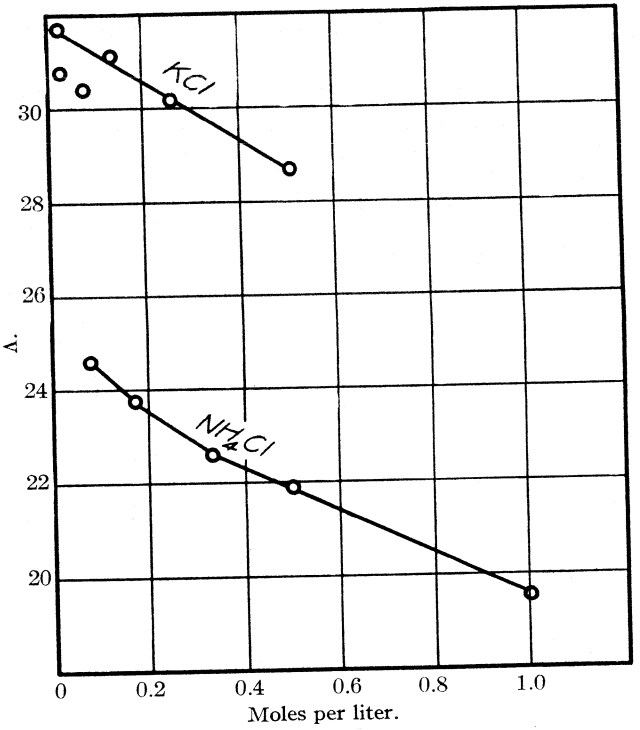


Fig. 2.

Summary

1. Two methods of preparing relatively pure iodine monochloride are described. One is an improvement on traditional methods; the other is a new method.

2. Results of vapor pressure measurements indicate that iodine monochloride is a polar liquid.

3. Conductivity measurements show that iodine monochloride acts as a dissociating solvent on potassium and ammonium chloride.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE EFFECT OF ADSORBED GASES ON THE PHOTOELECTRIC EMISSIVITY OF IRON AND PLATINUM

BY A. KEITH BREWER

RECEIVED JANUARY 8, 1932 PUBLISHED MAY 7, 1932

The present research was undertaken to determine, as far as possible, the physical state of gases adsorbed on metallic surfaces, with the hope in view that this knowledge will contribute to our understanding of surface catalysis. The metals chosen for investigation were iron and platinum, while the gases used were nitrogen, hydrogen, ammonia, helium and oxygen. Thus the study comprises both excellent and poor catalysts for the synthesis of ammonia, as well as reactive and poisonous gases.

Apparatus.—The apparatus, illustrated in Fig. 1, is essentially the same as that described in previous papers,[1,2] except that a Pliotron FP 54 four element vacuum tube was used in place of the Compton electrometer. The current sensitivity was 4.35×10^{-15} amp. per cm. galvanometer deflection; it was possible to read currents accurately from 5×10^{-16} to 10^{-11} amp. The sensitivity can be increased considerably beyond this point but it was not necessary in this research.

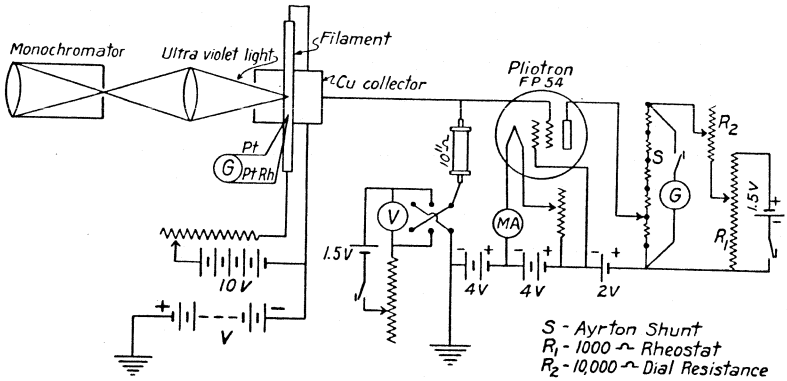


Fig. 1.

Method of Procedure.—It was found necessary to take special precautions for the removal of oxygen and water vapor from the gases. The nitrogen, hydrogen and helium were passed slowly through a tube filled with freshly reduced copper heated to 500°, dried with liquid air, and then stored in a balloon flask containing a tungsten filament. The gases were kept in contact with the incandescent tungsten for a day. The balloon flask was connected to the main system by a stopcock followed by a mercury seal to prevent grease contamination during operation. The gases were again passed through liquid air before entering the photoelectric tube. The ammonia was taken from a tank of liquid ammonia that had stood in contact with metallic potassium for years.

[1] A. Keith Brewer, *Phys. Rev.*, **38**, 401 (1931).

[2] A. Keith Brewer, THIS JOURNAL, **53**, 74 (1931).

The entire system was thoroughly flamed out before starting a series of runs. The filament was then heated to redness in about 2 cm. of hydrogen for an hour, after which the system was again flamed out and the filament heated *in vacuo* until it showed the normal long wave length limit, *i. e.*, a just detectable emission with λ2536 for iron and a small emission with λ2653 for platinum. An iron surface is readily purified but platinum requires considerable heating at 800° to give anything like a constant threshold, due to the difficulties of removing absorbed hydrogen.

Results with Iron

The factors given special attention in making this study were the effect of the gases on the intensity of emission as well as on the shift in the photoelectric threshold, the character of the wave length *vs.* current curves, and the effect of temperature on the sensitivity.

The data were taken with an accelerating potential of 9 volts plus the contact potential difference between the filament and collector; stopping potential measurements showed the latter to be near +1 volt. This potential was below the ionization potential of any of the gases studied so the possibility of ionization by collision did not exist.

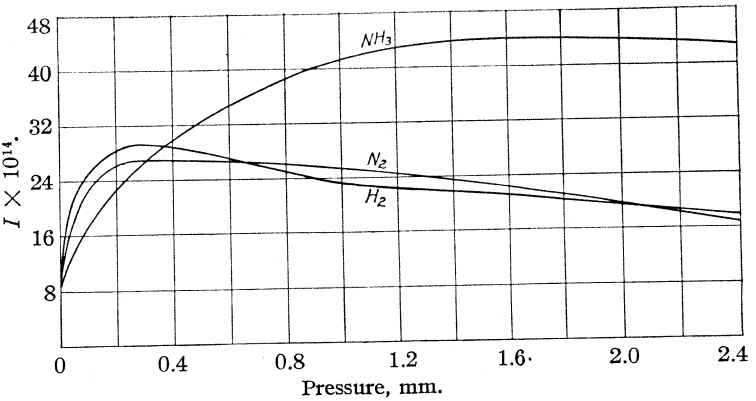


Fig. 2.—The effect of gases on the photoelectric emissivity of iron: *V*, 9; λ, 2300; temp., 215°C.

Gas	*V*	λ	Temp.
NH_3	9	2300	215°C.
H_2	9	2300	215°C.
N_2	9	2300	215°C.

The effects of various pressures of hydrogen, nitrogen and ammonia on the emissivity of iron are shown in Fig. 2. The measurements were all extended to 10 cm. pressure; the photoelectric current decreased only slightly with increasing pressure above 2.0 mm.

The emissivity curves for nitrogen and hydrogen are very nearly identical over the entire pressure range; the ammonia curve is distinctive in that the current enhancement for low pressures is less than that for nitrogen or hydrogen, while for high pressures it is materially greater. Oxygen

behaves quite differently in that when present in the most minute traces it materially lowers the emissivity. For instance, nitrogen, when passed slowly through a freshly reduced copper deoxidizer at 500° and thereafter held in contact with glowing tungsten for about fifteen minutes, still contained enough oxygen to give an emissivity definitely lower than nitrogen which had been held in contact with incandescent tungsten for ten hours. The amount of oxygen on the surface necessary to give a lowering of the threshold was too small to be estimated with any degree of precision.

Voltage *vs.* current measurements showed saturation to exist at pressures below the maximum points on the pressure *vs.* current curves; at higher pressures the current increased gradually with the voltage until ionization by collision set in, whereupon rapid increases were observed. At 10 cm. the current increase was but slightly less than linear with respect to voltage. At pressures below 0.4 mm. saturation was obtained for 2.0 volts accelerating potential.

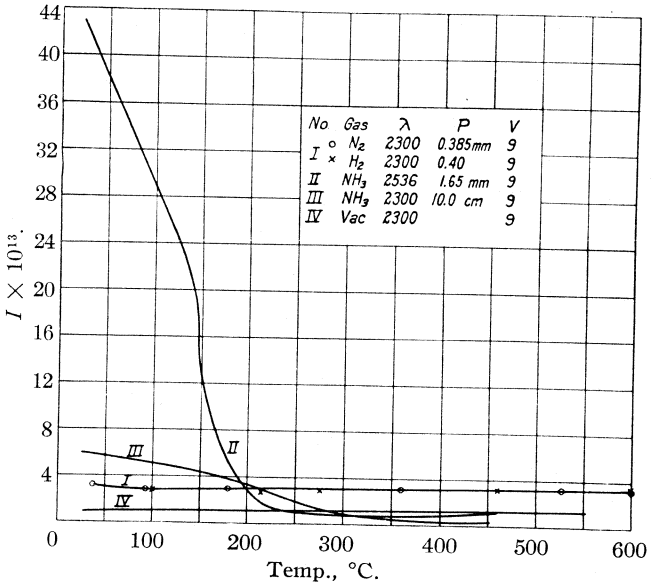


Fig. 3.—The effect of temperature on the photoelectric emissivity of iron in gases.

The effect of temperature on the emissivity is illustrated in Fig. 3. Line 1 shows nitrogen and hydrogen to be almost identical in their behavior, the points for nitrogen being just slightly the higher. Line IV is typical of the results obtained when the pressure becomes too low to read on the McLeod gage, without making any attempt to degas the iron; the curve for degassed iron is similar but somewhat lower. The temperature coefficient for ammonia differs from that for nitrogen and hydrogen, since it ab-

normally increases the emissivity at temperatures below 200°. The curves are all completely reversible when the products of decomposition of ammonia were not allowed to accumulate.

The effect of gases on the long wave length limit is suggested by the character of the lines in Fig. 4. The curves are distinctly different from those obtained in the absence of a gas in that the metal does not have a sharp long wave length limit. Thus the lines in Fig. 4 skirt the wave length axis to no definite limit and do not end sharply at some specific wave length.

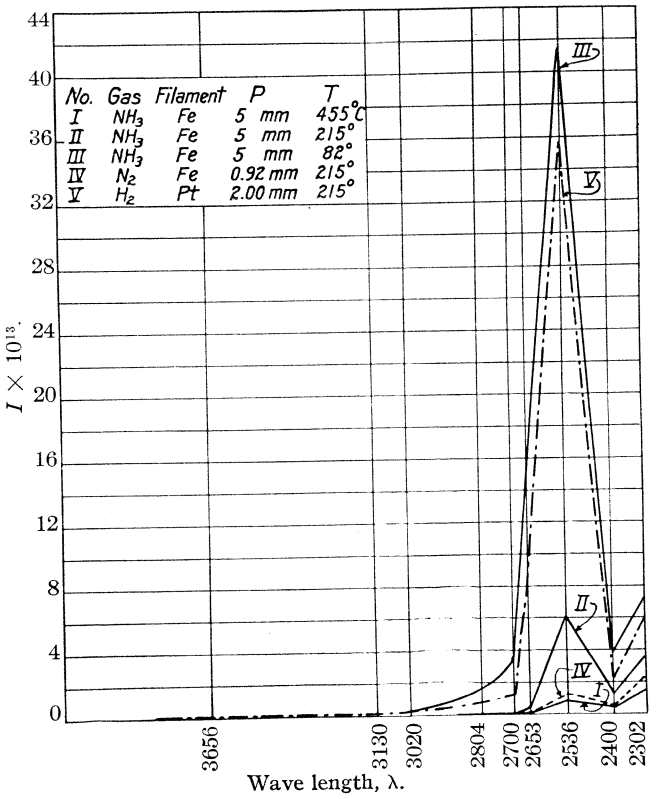


Fig. 4.—Characteristic wave length *vs.* emissivity curves.

Pure iron in a vacuum showed a just detectable emission for λ2536[1,2] with a threshold near 2575 Å. In the presence of hydrogen the emissivity became negligible below λ2750 and for nitrogen below λ2802. Ammonia, however, gave a definite emissivity for λ3650, the threshold lying near the limit of the visible, about 4000 Å. Expressed in equivalent volts the approximate thresholds are: vacuum 4.8 volts, hydrogen 4.5 volts, nitrogen, 4.4 volts and ammonia 3.1 volts. These values are for pressures just

above the maximum point in the curves shown in Fig. 2 and for room temperature.

The long wave length limit in oxygen when present even in small amounts was too low to be measured. One millimeter of nitrogen containing near 0.01% oxygen dropped the threshold to near 2300 Å.; *i. e.*, it raised the work function from 4.8 volts to more than 5.4 volts. Under these conditions there was just about enough oxygen present in the entire system to cover the filament with a monomolecular layer. Since the lowering of the threshold took place immediately upon the introduction of the oxygen and since the system was so designed that the probability of the average oxygen molecule striking the filament surface was very small, the amount of the surface covered by oxygen must have been only a very small fraction of a monomolecular layer. Continued heating in gas of this composition lowered the threshold to a point where an emissivity could no longer be detected.

Results with Platinum

The effect of gas pressure on the emissivity was investigated between 10 cm. and the best vacuum that could be obtained. Characteristic results are plotted in Fig. 5. The emissivity curves given are for λ2300 Å. and for λ2700 Å.; the temperature of the filament was 215°. The same gas was used throughout each series of runs except for ammonia, where the system was evacuated and refilled between each pressure measurement to prevent the accumulation of any products of decomposition.

The data were all taken starting with high pressures and temperatures working toward the low, though after the filament had once been heated to the maximum temperature used, all points were reproducible when approached from either side.

The curves show that the emissivity increases rapidly with the advent of gas to a maximum in the neighborhood of a few tenths of a millimeter pressure, after which it decreases slowly with pressure over the entire range investigated; the change between 1 and 10 cm. is very slight. The location and sharpness of the maximum depend both on the gas and on the wave length of the light. To illustrate, hydrogen always shows a sharp maximum for wave lengths considerably removed from the threshold, the sharpness gradually disappearing toward longer wave lengths. This is shown in the hydrogen curves for λ2300 and λ2700.

The emissivity in hydrogen, as is shown by Fig. 5, is large compared to that in nitrogen, ammonia, helium and oxygen. This enhanced emissivity is accompanied by a shift in the long wave length limit toward the red, as is illustrated by magnitude of the currents obtained with λ2700 in the various gases. The threshold for oxygen lies near 2225 Å., for helium is near 2650 Å. and for nitrogen and ammonia it is near 2750 Å.

Hydrogen, on the other hand, gives the characteristic curve of a highly composite surface, as will be seen by line V in Fig. 4. Under most advantageous conditions an emission could just be detected with λ4078, although λ3650 is usually near the limit. The possibility of the observed currents being due to scattered light was removed by placing suitable screens in the path of the ultraviolet light before entering the monochromator.

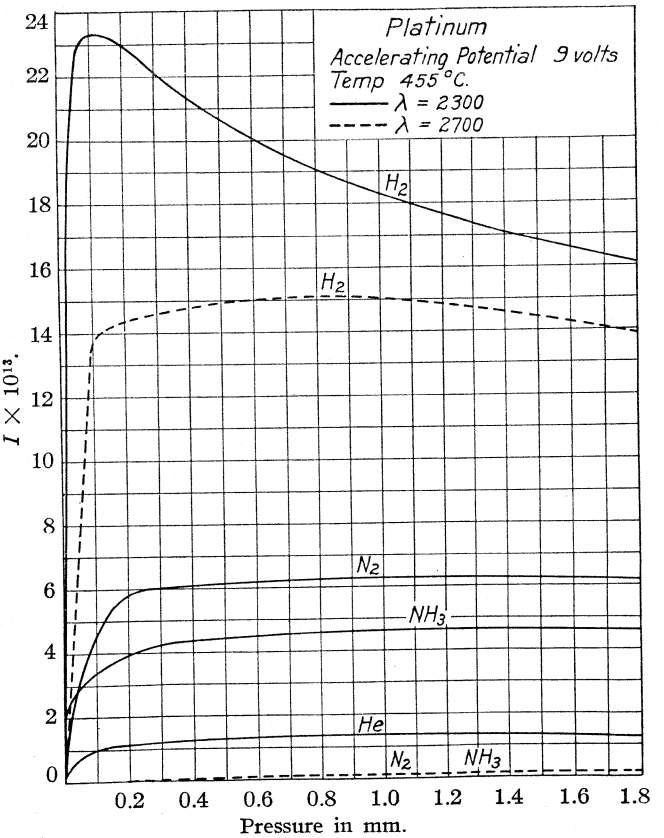


Fig. 5.—The effect of gases on the photoelectric emissivity of platinum.

The decrease in emissivity observed in oxygen is interesting in that it is not due to the normal gas molecules; the effect of oxygen on a cold filament is not materially different from that of nitrogen. As the filament is heated, the photoelectric current rapidly drops, the threshold finally shifting to below 2225 Å. This rapid shift in threshold is most pronounced when the filament has previously been heated in hydrogen for some time; under such conditions it is accompanied by the formation of water within the tube, even though the filament has been thoroughly glowed in a vacuum

before introducing the oxygen. Apparently the first rapid shift in threshold is due to the removal of hydrogen from the platinum by the oxygen, followed subsequently by a combination between oxygen and platinum, since an appreciable emissivity cannot again be obtained without reducing in hydrogen.

The effect of temperature on the emissivity in various gases is illustrated in Fig. 6. In general, the data were taken while going from higher to lower temperatures, but the effects were all perfectly reversible. Curve 6 for the evacuated system is not for outgassed platinum but represents the condition where the pressure is too low to be read by a McLeod gage and where the filament is being lowered from 600° to room temperature.

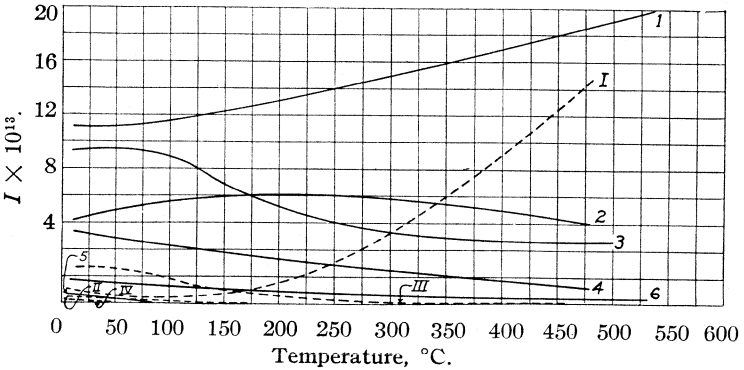


Fig. 6.—The effect of temperature on the photoelectric emission of platinum in gases.

Curve	Gas	λ	*P*, mm.	Curve	Gas	λ	*P*, mm.
1	H_2	2300	0.435	III	NH_3	2700	0.80
I	H_2	2700	.435	4	He	2300	.485
2	N_2	2300	1.7	IV	He	2700	.485
II	N_2	2700	1.7	5	O_2	2300	10.00
3	NH_3	2300	0.80	6	—	2300	vac.

Curves 4 and 6 for helium and for the evacuated system show a small enhancement in emissivity with decreasing temperature, while Curve 1 for hydrogen shows a large positive temperature coefficient. Nitrogen exhibits only a small temperature effect. The ammonia curve is characteristic of this gas in that there is a pronounced increase in emissivity as the temperature drops from 200 to 100°, while above and below these points the temperature coefficient is small; the effect, however, is much less than for iron.

The emissivity in gas mixtures could be analyzed in a few instances. In the case of hydrogen on platinum the addition of nitrogen had no appreciable effect. The addition of nitrogen or hydrogen to ammonia had no effect on the enhancement of the emissivity from iron. For platinum,

on the other hand, the addition of hydrogen to ammonia raised the emissivity to a point corresponding to pure hydrogen.

Discussion of Results

No ambiguity can exist regarding the nature of the wave length *vs.* current curves, as illustrated in Fig. 4. They are distinctly the type of curves obtained only on composite surfaces;[1,2] indeed, these curves can be exactly duplicated by those previously obtained from pure iron on which various amounts of potassium ions had been deposited. In the neighborhood of 0.5 mm. pressure the wave length characteristic for iron in hydrogen coincides with line 2, Fig. 2, of the previous communication[1] for an iron surface 0.002 covered with potassium ions. The results for nitrogen fall between Curves 2 and 3, and correspond with a surface 0.003 covered, while the maximum effect obtained with iron in ammonia corresponds to line 7 for a surface 0.02 covered with potassium ions.

In continuing the comparison between the photoelectric emission in gases and on composite surfaces it is interesting to note that for low gas pressures the sensitivity of the surface increases almost proportionally to the pressure, while Fig. 3 of the previous article shows the emission to be proportional to the concentration of potassium ions on the iron when the fraction of the surface covered is less than 0.04. The failure of the proportionality between pressure and current to extend over a wider range is doubtless due to three causes. First, saturation cannot be obtained above 0.4 mm. pressure. Second, the sensitivity is lowered by the presence of neutral gas particles, whether atoms or molecules, covering the surface. Third, the presence of space charges in the layers of gas near the surface materially lowers the emission current.

The physical status of the composite surface, capable of giving the observed effect, necessarily entails some degree of speculation. It safely may be said however, that since it affects the work function of the surface for escaping electrons, it is necessarily electrical in nature. Several possibilities may exist: a small percentage of the gas molecule striking the surface may become ionized by the surface forces; the surface may be covered with a highly polar layer of gases, in the "incipient ionization" stage as described by Sir J. J. Thomson;[3] or a state of dynamic equilibrium may exist in which the gas is in all degrees of dissociation from normal molecules to complete ions, as prescribed by probability.

Little if anything of a quantitative nature is known regarding the effect of polarized or "incipiently ionized" molecules on the work function, hence it cannot be told whether such a surface state will satisfy the demands of the emissivity curves. Since the curves are identical with those obtained for surfaces sparsely covered with ions, the most probable inter-

[3] J. J. Thomson, "The Electron in Chemistry," J. B. Lippincott, Co., 1923.

pretation to adopt is that a fraction of the gas molecule striking the surface is completely dissociated into ions; it is reasonable to assume that the ionized gas is present in various degrees of dissociation in dynamic equilibrium with the ionized and normal molecules. In this connection, Kobosew and Anochin[4] compute the ionization potential of the average hydrogen molecule on platinum to be of the order of 4 volts.

The ionization of gases at metallic surfaces has long been recognized in thermionics. It was first pointed out by H. A. Wilson[5] and has been discussed in detail by O. W. Richardson[6] from the point of view of thermionic emission. Erikson[7] has shown that the mobilities of the ions from alkali-free platinum in air are identical with air ions and concludes that the ions most probably come from gas molecules dissociated on the platinum.

Schmidt[8] has calculated the conditions under which hydrogen may be dissociated into ions at metallic surfaces and has shown his deduction to be in agreement with the observed facts found in the catalytic hydrogenation of organic compounds. The writer has shown certain correlations between temperature and work function in thermionic emission in gases,[9] and has proposed a mechanism for surface catalysis in which the problem is considered as a special case of thermionic emission in gases.[10] The present results furnish another method of attacking the problem of ionization of gases at metallic surfaces wherein it is possible to estimate the degree of ionization over a definite pressure region and also to show the effect of the adsorbed ions (adions) on the work function of the surface.

The condition established by the presence of ions adsorbed on a conducting surface may easily be understood from the following considerations. Becker[11] has shown from thermionic studies that barium ions adsorbed on tungsten behave in a manner analogous to that which would result from a grid placed at an atomic diameter from the surface and charged positively with respect to the surface. This same analogy is even more strikingly shown in the recent photoelectric studies. The effect of the adsorbed ions is exactly that of a grid covering the surface where the grid spacings correspond to the distance between the ions; thus for conditions where the fraction of the surface covered by ions is small the *grid spacings* are large compared to the distance between the grid and the surface.

On leaving a conductor an electron must do a certain amount of work

[4] Kobosew and Anochin, *Z. physik. Chem.*, **13**, 18 (1931).

[5] H. A. Wilson, *Phil. Trans. Roy. Soc.*, **A197**, 415 (1901).

[6] O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., New York.

[7] H. A. Erikson, *Phys. Rev.*, **26**, 625 (1925).

[8] O. Schmidt, *Z. physik. Chem.*, **118**, 195 (1925).

[9] A. K. Brewer, *Proc. Nat. Acad. Sci.*, **13**, 592 (1927).

[10] A. K. Brewer, *J. Phys. Chem.*, **32**, 1006 (1928).

[11] J. A. Becker, *Trans. Am. Electrochem. Soc.*, **55**, 21 (1929).

against the image and intrinsic forces of the surface; this work may be expressed in equivalent volts, ϕ, which under ordinary conditions lies between 3 and 6 volts. In thermionics the value of ϕ is obtained directly from the Richardson equation, $I = AT^{1/2} e^{-e\phi/kT}$, while in photoelectrics it is given by the relation $\phi = h\nu_0 - \phi_0 e$, where ν_0 is the threshold frequency and $\phi = 12345/\lambda$.

The immediate effect of a positive grid near the surface is to lower ϕ_0 and hence to lower ν_0 by an amount depending on the strength of the field of the grid at the point of exodus of the electron; adsorbed negative ions will tend to raise the work function. In thermionics this point of exodus is where the work function is lowest, *i. e.*, where the grid field is the highest, hence close to the adsorbed positive ion. In photoelectrics, on the other hand, the electron leaves at whatever point the quantum strikes. If the distance between ions is large compared to an atomic diameter, the work function will vary over a wide range depending on whether the electron escapes from a point near the adion or at the maximum point removed. There is little possibility of an electron being emitted from the adion itself, since the second ionization potential of the ion requires more energy than is ordinarily available.

It is this variation in work function from point to point over the surface that is responsible for the shape of the wave length *vs.* current curves obtained for composite surfaces. ϕ_0 no longer has a definite value for the entire surface, but varies from point to point depending upon the nearness of the adsorbed ions. Thus the wave length *vs.* current curves do not have the sharp feet characteristic of pure surfaces but skirt the wave length axis for long distances.

The presence of comparatively few ions adsorbed on the surface has an extremely large effect on the work function of an emitter. When the fraction of the surface covered by K^+ ions is 0.001, the threshold is shifted from 4.8 to about 4.65 volts; a 0.01 fraction shifts ϕ to 3.9 volts, while 0.02 reduces it to 3.1 volts. The values given are derived from the point where the emission becomes detectable; the true threshold doubtless is materially lower, as will be seen from the peculiar shape of the wave length *vs.* current curves. While these values are for K^+ ions, they will not differ markedly for any singly charged ion. From the above it follows that the sphere of influence of an adsorbed ion is strong even at a distance of ten times the ionic radius. The chemical analogy of these considerations is that when the fraction of the surface covered by adsorbed ions is but 1% of the total, the critical increment for electrons is shifted by about 23,000 calories.

The marked inhibiting effect of minute traces of oxygen on the photoelectric emissivity is readily understood in the light of the above considerations. The oxygen, upon combining with the iron, is attached to the

surface in the form of negative ions. It is obviously impossible to apply a lattice structure to an iron surface so sparsely covered with oxygen; however, the linkage most probably resembles that in FeO, which has a sodium chloride structure. If the oxygen is on the surface in the form of O^{--} ions, an abnormally high increase in the work function per ion density would result.

Application to Surface Catalysis.—A quantitative application of these results to surface catalysis cannot be made at this time, since neither the rate of ion formation nor the distribution of ions for mixed gases can be told with certainty. From a qualitative point of view, however, these findings are in accord with the theoretical conclusions of Schmidt,[8] since the relative ionization of hydrogen appears to be much greater on platinum than on iron. Further, they are in general agreement with the ionic mechanism of catalysis presented by the writer some time ago.[10] This mechanism, which is a direct application of thermionic emission in gases to surface catalysis, has been materially simplified and strengthened by recent studies of chemical action in the glow discharge[12] wherein it has been shown that the reactivity of positive ions is high compared to that of other active states, that the reaction is always initiated by ions of only one of the reactants, and that the number of collisions an ion must make with neutral molecules for reaction to take place is small, being from 10 to 40. Thus it will be seen that a catalyst, on the basis of this mechanism, need produce ions of only the reacting gas to initiate the reaction.

Kunsman[13] has shown that iron is an excellent catalyst for the decomposition of ammonia while platinum is relatively poor. On the basis of the above mechanism, therefore, ammonia should be highly ionized on iron and only slightly on platinum. The results in general are in agreement with this point of view. The addition of hydrogen to ammonia had no appreciable effect on the emissivity of iron in ammonia, indicating that hydrogen does not replace ammonia at an iron surface. When hydrogen was added to ammonia on platinum, however, the emissivity rose to that for pure hydrogen; apparently it is the hydrogen which is the more dissociated on platinum. It is possible that the preferential adsorption of hydrogen by platinum is responsible for its low catalytic activity.

The glow discharge studies have shown that the synthesis of ammonia is initiated primarily by N_2^+ ions. The relatively high ionization of nitrogen on iron, combined with the fact that nitrogen had no appreciable effect on the emissivity from platinum in the presence of hydrogen, indicates that under the conditions of ammonia synthesis iron is the better source of N_2^+ ions and hence according to the ionic mechanism should

[12] Brewer and Westhaver, *J. Phys. Chem.*, **34**, 153, 2343 (1930); Brewer and Kueck, *ibid.*, **35**, 1281 (1931); Brewer and Miller, THIS JOURNAL, **53**, 2968 (1931).

[13] C. H. Kunsman, *ibid.*, **50**, 2100 (1928); **51**, 688 (1929).

be the better catalyst. Platinum, however, should be the better catalyst for reactions initiated by positive hydrogen ions. The glow discharge studies show the synthesis of water to be initiated by H_2^+ ions. The experimental results in both cases are in apparent conformity with the theory.

The pronounced effect exerted on the work function by the presence of only a sparse distribution of adsorbed ions on the surface, combined with the large sphere of influence about these ions, is of vital importance to any mechanism of catalysis in which electrical forces are involved. In thermionic emission it is generally felt that the electrons escape at the points on the surface having the lowest work function. Since the rate of chemical action is expressed by the same mathematical equations as is the rate of thermionic emission of ions, it seems reasonable to suppose that the reaction takes place primarily at the points of lowest critical increment. The results of Kunsman on the decomposition of ammonia on various catalysts are in qualitative agreement with this contention. These considerations suggest a very simple mechanism for action of promoters and poisons. Ions on the surface that lower the work function serve as promoters while those that raise the work function behave as poisons. An illustration of this may be had from the observed effect of oxygen ions on raising the work function of iron; oxygen is a pronounced poison in the ammonia reaction.

In line with the above point of view it is interesting to note that in every case investigated the thermionic and photoelectric work functions for degassed surfaces have been shown to be identical. Warner[14] has studied tungsten, DuBridge platinum[15] and Cardwell[16] iron, cobalt and tantalum.

Since the thermion escapes at the point of lowest work function while the photoion escapes wherever the quantum strikes, these findings are conclusive proof that the field of force for a degassed surface is uniform over the entire surface. This suggests the possibility that the phenomena generally attributed to active points on catalytic surfaces may in reality be due to the large fields of force about the ions adsorbed on the surface.

The writer is indebted to Dr. C. H. Kunsman for the interest he has taken in this research.

Summary

An investigation of the photoelectric properties of iron and platinum in the presence of various gases shows that the metals do not exhibit the characteristic properties of a pure metal as is found under good vacuum conditions but rather possess the properties of composite surfaces. In-

[14] Warner, *Phys. Rev.*, **38**, 1871 (1931).

[15] DuBridge, *ibid.*, **31**, 263 (1928).

[16] Cardwell, *ibid.*, **38**, 2033 (1931); *Proc. Nat. Acad. Sci.*, **14**, 439 (1928).

deed, it is possible to duplicate exactly the photoelectric characteristics of these metals by curves taken *in vacuo* in which the surface of the metal is partially covered with adsorbed ions. Taking curves of known ion density as a standard, the degree of dissociation of the different gases into ions is estimated.

Threshold measurements on surfaces of known ion density show the field of influence about an ion to extend out to many times its normal radius; at ten times the ion radius the field is of appreciable magnitude. This is true for both positive and negative ions, although the effect is opposite in sign.

It is suggested that the large field of force about the adsorbed ions might account for the phenomena generally attributed to "active centers," and, further, that the large effect of adsorbed ions on the work function of the surface might be responsible for poisoning and promoter action.

The observed ionization of nitrogen, hydrogen and ammonia on iron and platinum surfaces is shown to be in accord with an ionic mechanism for surface catalysis and with the activation results obtained in the glow discharge.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY AND ENTROPY OF THALLOUS NITRATE FROM 17 TO 300° ABSOLUTE. THE ENTROPY AND FREE ENERGY OF NITRATE ION

BY WENDELL M. LATIMER AND J. ELSTON AHLBERG[1]

RECEIVED JANUARY 11, 1932 PUBLISHED MAY 7, 1932

In a previous investigation[2] the entropy of nitrate ion was calculated from data on barium nitrate. A similar evaluation of the entropy of nitrate ion has now been made from data on thallous nitrate. A discrepancy of 1.6 entropy units has been found between the two results. As in the previous work in this field the entropy of the solid salt at 25° has been determined from specific heat measurements carried down to the temperatures of liquid hydrogen. The accuracy of these measurements is considerably greater than the discrepancy found in the two calculated values for the entropy of nitrate ion and attention must therefore be directed to a re-examination of the existing data which have been used in the barium nitrate evaluation.

[1] Du Pont Fellow in Chemistry, 1929–1930.

[2] (a) W. M. Latimer and J. E. Ahlberg, *Z. physik. Chem.*, **148**, 464 (1930). For references to details of theoretical and experimental method, see (b) Latimer and Buffington, THIS JOURNAL, **48**, 2297 (1926); (c) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); (d) Latimer and Kasper, *ibid.*, **51**, 2293 (1929).

Material.—The thallous nitrate was a mixture of two "C. P." samples from Eimer and Amend and C. A. F. Kahlbaum. This material was filtered and recrystallized four times. It was then dried at 65° for three weeks. The average of six precipitations with potassium iodide gave 100.0% of the theoretical amount of thallous iodide.

Thallous nitrate undergoes a transition at about 75° and the long heating at 65° was carried out to ensure complete transformation into the form stable at low temperatures. The authors are greatly indebted to Professor Linus Pauling and Dr. J. H. Sturdivant of the California Institute of Technology, who have made x-ray examinations of our sample and report that it gives a powder photograph which is identical with that of the low temperature modification.

Heat Capacity Measurements.—The measurements were made with a calorimeter and cryostat similar to that previously described.[2c] Due apparently to repeated cooling, the bakelite, which cements the gold wire of the resistance thermometer to the walls of the calorimeter, loosened slightly during the course of the measurements and this gave rise to somewhat higher temperature heads during the energy input than had been previously obtained with this calorimeter. The maximum error which might have arisen from this source is less than 1% up to 140°K. and less than 3% from 140 to 300°K.; however, we believe it to be considerably less.

TABLE I

HEAT CAPACITY OF THALLOUS NITRATE (MOLECULAR WEIGHT 266.40)

Mean T, °K.	ΔT	C_p/mole in cal./deg.	Mean T, °K.	ΔT	C_p/mole in cal./deg.
16.45	4.307	2.964	101.71	5.376	15.67
20.52	3.109	4.166	108.68	5.831	16.07
24.44	2.725	4.965	116.98	5.943	16.42
27.95	3.218	5.892	130.25	6.550	17.03
31.35	2.897	6.647	137.92	6.123	17.31
35.22	2.537	7.607	149.85	6.395	17.77
39.94	6.100	8.623	162.78	6.302	18.19
45.29	4.668	9.649	174.79	6.966	18.82
49.55	3.456	10.43	182.43	7.585	19.09
52.91	3.020	11.06	197.32	6.130	19.59
59.49	3.677	12.00	211.64	6.905	20.09
60.33	4.156	12.12	226.53	6.915	20.62
64.51	4.202	12.64	242.59	7.016	21.28
69.19	4.718	13.21	250.52	6.709	21.63
74.22	4.582	13.74	258.40	7.739	21.91
79.34	4.997	14.20	265.25	5.638	22.21
84.54	5.229	14.68	272.38	8.312	22.60
90.02	5.406	14.97	281.69	7.736	22.91
95.90	5.833	15.36	290.60	7.295	23.43

Entropy of Thallous Nitrate.—Figure 1 is the plot of C_p against log T from which the entropy has been obtained by the graphical integration

$S = \int_0^T C_p \, d \ln T$. A summary of the entropy calculation is given in Table II.

TABLE II

CALCULATION OF THE MOLAL ENTROPY OF THALLOUS NITRATE

0–16.45°K. extrapolation	1.16
16.45–298.1°K. graphical from data	36.96
Entropy of thallous nitrate	38.1 E. U.

The maximum error arising from the cooling corrections is less than 0.6 entropy unit. The average deviations of the points on the C_p curve give, however, a calculated error of about 0.1 unit.

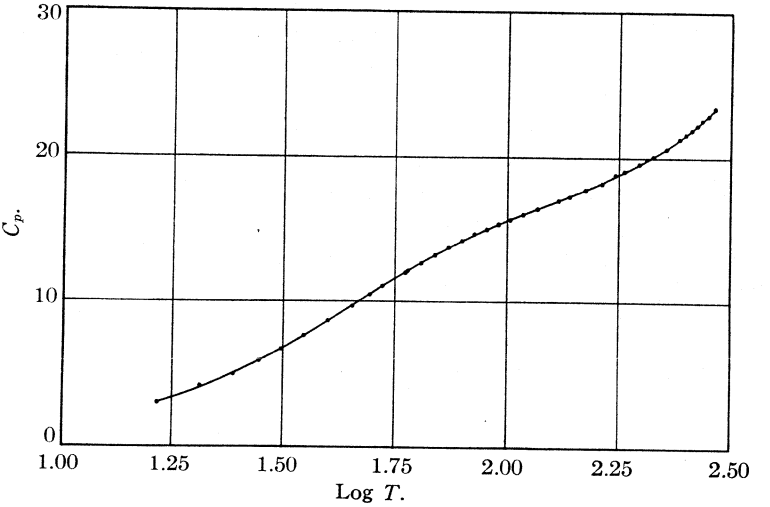


Fig. 1.—Molal heat capacity of thallous nitrate.

Entropy of Nitrate Ion.—The solubility of thallous nitrate at 25° is 0.434 M.[3] The relative conductivities of solutions of thallous and silver nitrates and also activity data by Lewis and Randall indicate that the activity coefficient of thallous nitrate is slightly lower than that of silver nitrate, for which Lewis and Randall[4] give 0.55 at 0.434 M. Hence we have chosen the value $\gamma = 0.50$ and calculate for the free energy of solution

$$\Delta F^\circ = -RT \ln (\Delta m)^2 = 1790 \text{ cal.}$$

Combining this with Thomsen's value for the heat of solution of thallous nitrate, $\Delta H = 9970$, we obtain for the entropy change, solid to form hypothetical one molal solution

[3] Data from Berkeley, *Phil. Trans. Roy. Soc., London*, **203**, 89 (1904); and Étard, *Ann. chim. phys.*, **2**, 503 (1893).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = \frac{9970 - 1790}{298.1} = 27.4 \text{ E. U.}$$

This gives for the sum of the entropies of nitrate and thallous ions, using the value obtained for the entropy of the solid, 27.4 + 38.1 = 65.5 E. U.

We now wish to express the entropy of nitrate ion in respect to $H^+ = 0$ and the most reliable method of carrying out this calculation employs the data for hydrochloric acid and thallous chloride. These have been summarized in Table III.

TABLE III

THE ENTROPY OF HYDROCHLORIC ACID AND THALLOUS CHLORIDE IN AQUEOUS SOLUTIONS

	Entropy of substance 298.1°K.	ΔH of soln., cal.	ΔF of soln., cal.	ΔS of soln., E. U.	Sum of ionic entropies, E. U.
HCl	44.7[5]	−17,750[7]	−8604[8]	−30.5	14.0
TiCl	25.8[6]	−10,100[7]	5086[8]	16.8	42.6

From these values the entropies, referred to $S^\circ_{H^+} = 0$ are: Cl^-, 14.0 and Tl^+, 28.6. Using the sum of the entropies of thallous and nitrate ions as given above, we then calculate for the nitrate ion $S^6_{298.1} = 65.6 - 28.6 = 36.9$ E. U. In our previous determination[2] based upon analogous calculations for barium nitrate, we obtained 35.3 E. U. for nitrate ion. We believe that the value from thallous nitrate is accurate to 1 E. U., *i. e.*, to 300 cal. and that the discrepancy probably is due to errors in the data used to calculate the entropy of barium ion. Investigations are under way to check these quantities. It might also be mentioned that the theoretical evaluation of the entropy of aqueous ions by Latimer and Kasper[2d] has indicated that the experimental value for barium ion is too high.

Free Energy of Nitrate Ion.—For the heat of the reaction

$$\frac{1}{2} H_2 + \frac{1}{2} N_2 + \frac{3}{2} O_2 = H^+ + NO_3^-$$

Berthelot gives $\Delta H = -48{,}800$ cal. and Thomsen −49,100 cal. These values are for 18° but may be corrected to 25° since the specific heats of all the substances are known. The average value for $\Delta H_{298.1}$ then becomes −49,400. Using the entropies: H_2, 31.2;[9] N_2, 45.8;[10] O_2, 49.0;[11] H^+, 0 and NO_3^-, 36.9, we calculate $\Delta S = 36.9 - 15.6 - 22.9 - 73.5 = -76.1$. With the value for the heat of the reaction, the free energy then becomes

[5] Giauque and Overstreet, THIS JOURNAL, **54,** 1731 (1932).

[6] Calculation by Rodebush and Rodebush, "International Critical Tables."

[7] "International Critical Tables." The value for hydrochloric acid has been corrected to 25° using the heat capacity values given by Rossini, *Bur. Standards J. Research,* **7,** 47 (1931).

[8] From data in Lewis and Randall, Ref. 4, modified by recent work of Randall and Young, THIS JOURNAL, **50,** 989 (1928), and Randall and Vietti, *ibid.*, **50,** 1526 (1928).

[9] Giauque, *ibid.*, **52,** 4816 (1930).

[10] Giauque and Clayton, to be published.

[11] Giauque and Johnston, THIS JOURNAL, **55,** 2300 (1929).

$\Delta F^\circ = -49{,}400 - (298.1 \times -76.1) = -26{,}700$ cal. This is an excellent agreement with the Lewis and Randall[4] value $\Delta F^\circ = -26{,}500$ cal.

Entropy of Nitrite Ion.—We may make use of the values given by Lewis and Randall for ΔF° and ΔH° of the reaction

$$2AgNO_2(s) = Ag^+ + NO_3^- + Ag + NO(g)$$

and the known entropies of the reaction products, to calculate the entropy of solid silver nitrite. This we find to be 27.7. From this value together with the free energy and heat of solution of silver nitrite and the entropy of silver ion we calculate for the entropy of nitrite ion, 24.0 E. U. The direct determination of the entropy of solid silver nitrite will afford an interesting check upon the entropies of both nitrate and nitrite ions.

Entropy of Hydration of Nitrate.—It is of interest to compare the entropy of nitrate, 36.9, with that of carbonate, −14. Since the entropies of the two substances as gases should be very nearly the same, the difference must arise from the effect upon the entropy of the water molecules of the double charge on the carbonate. Latimer and Kasper[2d] have found for the simple ion that the entropy of hydration is $22\ e^2/r$ E. U. where e is the charge on the ion and r the distance in Ångström units from the center of the ion to the center of the water dipoles surrounding the ion. Estimating r as approximately 3 Å. for carbonate and nitrate would lead to a difference of only 30 E. U. between the two ions instead of the 51 units found. It seems probable that part of the discrepancy is due to the dissymmetry of these ions, which permits one or more water molecules to be drawn very much closer to the center of the ion. The calculation also assumes that the effective change is located at the center of the ion cavity whereas actually the field outside the ion probably corresponds to a more complex distribution.

The authors wish to express their appreciation to Professor Linus Pauling and Dr. J. H. Sturdivant for their x-ray examination of the sample of thallous nitrate.

Summary

The specific heat and entropy of thallous nitrate has been determined from 17 to 300° absolute. These values have been employed in a calculation of the entropy and free energy of nitrate ion.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A GRAVIMETRIC METHOD FOR THE SEPARATION AND DETERMINATION OF TITANIUM[1]

BY HAL TRUEMAN BEANS AND DOROTHEA R. MOSSMAN

RECEIVED JANUARY 22, 1932 PUBLISHED MAY 7, 1932

Existing methods for the separation of titanium from its common associates leave much to be desired from the standpoint of accuracy, ease of manipulation and speed. A perusal of the monograph "Titanium" by William M. Thornton is convincing evidence that a method for the determination of titanium in the presence of other elements, which avoids long and tedious separations and does not produce a gelatinous precipitate, is greatly needed.

Under proper conditions, a crystalline salt of titanium is quantitatively precipitated by potassium iodate, no precipitate being produced with aluminum, calcium, magnesium, nickel, phosphorus and chromium, elements which are commonly associated with titanium in ores. With slight modifications the method effects a separation of titanium from zirconium and manganese. It is necessary, however, that iron be removed previous to the determination of titanium. This is readily accomplished without modification of the method in any essential.

Reagents and Solutions

Titanium.—Titanium sulfate solutions were prepared by dissolving twice recrystallized potassium fluotitanate in sulfuric acid and heating to dense fumes of sulfur trioxide. Water was then added to obtain the desired concentration and the solutions were standardized by the precipitation of titanium hydroxide with ammonium hydroxide. The solutions used contained approximately 0.1 g. of TiO_2 in 50 cc. of solution and were 1.2 *N* with respect to sulfuric acid.

Zirconium.—A solution of C. P. zirconium nitrate which was 0.3 *N* with respect to sulfuric acid was prepared and standardized by precipitation with ammonium hydroxide. The solution was tested qualitatively and found to be free from iron and titanium. The hafnium content of this solution is not known and was not investigated.

Other Elements.—Solutions of the following C. P. salts, alum, calcium chloride, magnesium chloride, nickel chloride, iron chloride, manganous sulfate, primary potassium phosphate (recrystallized), ammonium vanadate, sodium chromate, were used as sources of these elements.

Potassium Iodate.—C. P. grade.

Thirty per cent. Hydrogen Peroxide.—Merck's Superoxol.

The Quantitative Determination of Titanium.—The procedure for the determination of titanium, employing the optimum conditions, follows. To 50 cc. of the standard solution, there was added 27 cc. of concentrated nitric acid and the volume made up to 200 cc. The reagent was prepared

[1] From the thesis submitted by Dorothea R. Mossman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1930. Original manuscript recieved August 29, 1931.

by dissolving 10 g. of potassium iodate in 100 cc. of water containing a few drops of nitric acid. This small concentration of nitric acid prevents the precipitation of potassium iodate when the solution cools. The reagent was added to the titanium sulfate solution slowly and with stirring, at room temperature. The precipitate was allowed to stand for about one hour, stirring now and again until the iodate precipitate changed from a flocculent to a dense crystalline form, and then it was washed five times by decantation with 20-cc. portions of a 2% solution of potassium iodate which contained 6 cc. of concentrated nitric acid to every 100 cc. of solution. The filter paper and precipitate were then transferred to the original beaker, 15 cc. of concentrated hydrochloric acid added and the filter paper macerated by the use of a stirring rod. A small volume of water was then added and sulfur dioxide bubbled through the solution until the brown coloration which first formed had completely disappeared. The volume was then adjusted to about 300 cc. and the sulfur dioxide expelled by boiling. The titanium was then precipitated by ammonium hydroxide, filtered, washed, ignited and weighed as titanium dioxide.

Determinations 1 through 20 of Table I show the results obtained when this procedure was followed. Determinations 21 through 35 show the results obtained when acids other than nitric and normalities other than 1.6 were used. Determinations 36 through 41 show the application of this method in determining amounts of titanium dioxide other than 0.1 g.

TABLE I

EXPERIMENTAL DATA

No.	Approx. wt. TiO_2, g.	Acid, cc.	Added acid	Total normality acid	KIO_3 added, g.	Number of analyses	Av. dev., %	Max. dev., %	Dev. of av. from standard, %
1–20	0.12	27	HNO_3	1.6	10	20	0.1	0.3	+0.01
21–22	.12	13	H_2SO_4	1.7	10	2	.1	.1	+ .2
23–24	.12	27	HCl	1.6	10	2	.05	.05	+ .05
25–26	.12	15	HNO_3	1.0	10	2	.05	.05	+ .05
27–28	.12	7	H_2SO_4	1.0	10	2	.2	.2	+ .1
29–30	.12	15	HCl	1.0	10	2	.05	.05	+ .15
31–33	.12	5.5	H_2SO_4	0.9	10	3	.03	.1	+ .1
34–35	.12	None added		.2	10	2	.05	.05	+ .05
36–37	.2	27	HNO_3	1.6	15	2	.02	.02	− .07
38–39	.05	27	HNO_3	1.6	10	2	.2	.2	.00
40	.01	27	HNO_3	1.6	10	1			1.0
41	.01	27	HNO_3	1.6	15	1			0.00

When the iodate precipitation was performed in solutions of greater acidity than those given in the table, addition of ammonium hydroxide to the filtrate showed the presence of titanium. Hence in solutions whose acid concentration is appreciably greater than 1.7 normal, the precipitation of titanium is incomplete.

It appears advisable when determining amounts of titanium dioxide very much greater or very much less than 0.1 g. to increase the quantity of potassium iodate added, in order to ensure rapid precipitation. Thus, in determination 40 of the above table, the precipitation, while complete, appeared only after standing for several days, whereas in determination 41 the precipitate appeared immediately in the dense very insoluble crystalline form.

Separation from Other Elements

Aluminum, Calcium, Magnesium and Nickel.—Preliminary tests having shown that aluminum, calcium, magnesium and nickel were not precipitated under the conditions of the determination, the maximum weight of the oxides of these elements that could be present without causing interference was then ascertained.

The separation of titanium from these elements using a single precipitation was accomplished by employing the iodate method as outlined above. In those determinations involving a second precipitation, the iodate precipitate was washed back into the original beaker with hot water, 25 cc. of concentrated hydrochloric acid was added and sulfur dioxide bubbled through the solution until the brown coloration disappeared. The sulfur dioxide was then completely expelled by boiling, the volume adjusted to 200 cc. and the titanium reprecipitated by the addition of 10 g. of potassium iodate dissolved in 100 cc. of water. From this point the procedure was similar to that already described. Table II shows the results thus obtained.

TABLE II

EXPERIMENTAL RESULTS

Approx. wt. of TiO_2, g.	No. of pptns.	Interfering element, g.	Number of analyses	Av dev., %	Max. dev., %	Dev. of av. from standard, %
0.1	1	0.1–0.2 Al_2O_3	9	0.1	0.3	−0.05
.1	1	.25 Al_2O_3	2	.05	.05	+ .35
.1	2	.35 Al_2O_3	4	.2	.3	+ .2
.1	1	.1 CaO	6	.1	.2	− .1
.1	1	.12–0.15 CaO	2	.15	.15	+ .6
.1	2	.2 CaO	4	.2	.3	+ .2
.1	1	.2–1.0 MgO	6	.1	.2	− .1
.1	1	.4 NiO	4	.15	.2	+ .1

The above results show that an accurate separation of 0.1 g. of TiO_2 from 0.2 g. of Al_2O_3, from 0.1 g. of CaO, from 0.4 g. of NiO and from very large amounts of MgO may be obtained. When a double precipitation is employed, the permissible quantity of Al_2O_3 and of CaO is increased to 0.35 g. and 0.2 g., respectively. The presence of larger quantities of the interfering elements than those shown in the table resulted in adsorption and consequent high results for the titanium oxide content.

Phosphorus, Vanadium and Chromium.—Phosphorus is frequently and vanadium and chromium occasionally are encountered in the analysis of titanic materials. Chromium, equivalent to 0.07 g. of CrO_3, did not produce a precipitate under the conditions of the determination. Vanadium, equivalent to 0.05 g. of V_2O_5, produced a bright red precipitate. However, 1 mg. of V_2O_5, which is as much as is likely to be present in a titanium ore, did not produce a precipitate. The iodate precipitation separated titanium from phosphorus very effectively as the results in Table III show.

TABLE III

TiO_2 taken, g.	TiO_2 found, g.	P_2O_5 present, g.
0.1023	0.1024	0.025
	.1024	.040
	.1020	.040

Manganese.—Manganese is notprecipitated by potassium iodate under the conditions of the experiment but a slight brown deposit, which appears to be manganese dioxide, forms in the course of an hour.

An attempt was made to keep the manganese in solution by observing Blum's precautions when precipitating with ammonium hydroxide, and results 1, 2 and 3 of Table IV were obtained. These results, therefore, corroborate Blum's statement[2] that oxidation and precipitation of manganese occurs so rapidly as to preclude quantitative separation and are in disagreement with the work of Lundell and Knowles.[3]

Correct results were obtained when the following procedure was used. The iodate precipitate was washed back into the original beaker by a stream of hot water and its solution effected by means of hydrochloric acid and sulfur dioxide; 1 cc. of a saturated ammonium bisulfite solution was added and the titanium then precipitated by the basic acetate method. Determinations 4 and 5 show the results obtained when 10 milligrams of Mn_3O_4 was present.

TABLE IV

No.	TiO_2 taken, g.	TiO_2 found, g.	Mn_3O_4 present, g.
1	0.1162	0.1186	0.020
2		.1169	.010
3		.1192	.010
4	.1147	.1148	.010
5		.1145	.010

Iron.—Iron, in small quantities, is completely precipitated by potassium iodate under the conditions of the experiment. When larger quantities of iron are present (*e. g.*, 0.1 g. of Fe_2O_3), the iron is incompletely precipitated. It was therefore necessary to remove iron previous to the precipitation of titanium, by Rothe's ether method, the modifications

[2] W. Blum, "Scientific Papers of the Bureau of Standards," No. 286, 1916.

[3] G. E. F. Lundell and H. B. Knowles, THIS JOURNAL, **45**, 676 (1923).

employed being those described by Barnebey and Isham.[4] Three ether extractions were performed. The aqueous layer was then transferred to a beaker, warmed to remove ether, and evaporated to 50 cc. to adjust the acid concentration. The volume was then brought to 200 cc. and the titanium precipitated as iodate. After the titanium iodate had changed form, it was washed as in the regular procedure, filtered, and washed back into the original beaker by means of hot water; 15 cc. of hydrochloric acid was added and sulfur dioxide bubbled in to effect the solution of the iodate precipitate. The excess sulfur dioxide was then expelled by boiling and the titanium precipitated by the basic acetate method using ammonium bisulfite to maintain the trace of iron, still remaining, in the reduced condition.[5] By means of this procedure the results in Table V were obtained.

TABLE V

No.	TiO_2 taken, g.	TiO_2 found, g.	Fe_2O_3 present, g.
1	0.1147	0.1148	0.12
2		.1146	.12
3		.1148	.2
4		.1149	.2
5		.1149	.2
6		.1145	.2
7		.1145	.2
8		.1148	.2
9		.1149	.2
10		.1147	.2
11		.1146	.2

Zirconium.—Existing methods for the separation of titanium and zirconium were found unsatisfactory. Davis[6] has given a few results on the use of sodium iodate as a precipitating reagent for zirconium in a nearly neutral solution, claiming that even in the presence of small quantities of acid the precipitation was incomplete. Because of the sensitivity of this reaction to slight changes in acidity, this method has been useless for practical purposes. Since Davis specifies merely an excess of sodium iodate, it was thought that this reaction might be used for quantitative purposes if as much as 10 g. of potassium iodate were used.

Zirconium was found to be partially precipitated by potassium iodate when the regular procedure, using a solution of acid normality 1.6, was employed. However, the precipitation was found to be complete in a solution which was 0.3 normal in respect to sulfuric acid. The iodate precipitate was redissolved by hydrochloric acid and sulfur dioxide and the zirconium reprecipitated by ammonium hydroxide. Determinations 1 through 4 of Table VI show the results obtained when this procedure was followed.

[4] O. L. Barnebey and R. M. Isham, THIS JOURNAL, **32**, 957 (1910).

[5] Wm. M. Thorton, *Am. J. Sci.*, [4] **37**, 173 (1914).

[6] I. Thomas Davis, *Am. Chem. J.*, **11**, 26 (1889).

Determinations 5 through 10 show analyses of solutions containing both titanium and zirconium. To these solutions 35 cc. of Superoxol was added and the volume made up to 200 cc.; 100 cc. of water containing 10 g. of potassium iodate was added to the solution and the precipitate allowed to stand for about three hours. The slight reaction which occurs between the hydrogen peroxide and the potassium iodate in no way interferes with the determination. After standing for three hours, the zirconium precipitate was filtered through a porcelain filter crucible and washed by decantation with 150 cc. of water containing 3 g. of potassium iodate and 3 cc. of Superoxol. Nine cc. of sulfuric acid was then added to the filtrate and the hydrogen peroxide expelled by boiling. An inverted funnel was suspended over the beaker to prevent loss by effervescence. When the hydrogen peroxide had been expelled the titanium precipitate appeared. The evaporation was continued down to a volume of 300 cc., when the beaker was removed from the flame and allowed to cool with occasional stirring. The remaining operations for the determination of titanium were the same as those already described.

In order to determine the zirconium, the precipitate was dissolved through the porous bottomed crucible by means of concentrated hydrochloric acid, followed by water. Sulfur dioxide was then bubbled through the solution for a minute or two and the excess sulfur dioxide expelled by boiling. Macerated filter paper was then added to the solution, the zirconium precipitated by ammonium hydroxide, washed with hot 2% ammonium nitrate solution, filtered and ignited to the oxide.

When more than 10 milligrams of zirconium dioxide was present it was found that the zirconium precipitate absorbed titanium to a large extent. However, since zirconium occurs only in small quantities in titanium ores, this method will be found applicable.

TABLE VI

No.	TiO_2 taken, g.	TiO_2 found, g.	ZrO_2 taken, g.	ZrO_2 found, g.
1			0.0150	0.0150
2				.0150
3			.0100	.0100
4				.0101
5	0.1023	0.1023	.0100	.0100
6		.1025		.0100
7		.1024		.0101
8		.1021		.0101
9		.1022		.0100
10		.1023		.0099

Determination of the Composition of the Iodate Precipitate.—Since there is no mention in the literature of a compound containing titanium and the iodate radical it was decided to determine, if possible, the composition of the precipitate.

The precipitate was washed about twenty times with pure water, in which it is insoluble. Difficulty was experienced in drying the precipitate as a slight decomposition with simultaneous discoloration of the compound took place very readily. However, one product which was fairly white was obtained by drying over phosphorus pentoxide in a vacuum for several days and another was obtained by drying in the oven at 60° to constant weight.

Weighed portions of the precipitate so prepared were used to determine the titanium and iodate content. Titanium was determined by basic acetate precipitation. Iodate was determined by reduction with potassium iodide and titration of the liberated iodine by sodium thiosulfate solution.

The results, which indicate that the compound is a double salt of formula $Ti(IO_3)_4 \cdot 3KIO_3$, are shown below

% Titanium found	% Iodate found
3.48 (dried over P_2O_5)	87.39 (dried over P_2O_5)
3.58 (dried over P_2O_5)	
3.56 (dried in oven)	88.32 (dried in oven)
3.40 (dried in oven)	88.35 (dried in oven)
Av. 3.50%	Av. 88.02%
Titanium calculated, 3.46%	Iodate calculated, 88.10%

Summary

A new gravimetric method for the determination of titanium has been described, in which the titanium is precipitated as a double potassium titanium iodate whose probable composition is $Ti(IO_3)_4 \cdot 3KIO_3$. The new method separates titanium quantitatively from a large number of the elements commonly occurring with it in ores, notably aluminum.

A procedure for the separation and determination of small amounts of zirconium from large amounts of titanium has been described.

New York City

NOTE

A Neutral Buffered Standard for Hydrogen Ion Work and Accurate Titrations Which Can be Prepared in One Minute

By Roger J. Williams and Carl M. Lyman

Most of the standard buffer solutions recommended in the literature must be prepared with considerable care and one cannot be sure of the result unless all the precautions of quantitative analysis are used. A simply prepared solution that can be relied on for standardizing quinhydrone electrodes, etc., is therefore much to be desired. Standardized buffer mixtures are on the market for this purpose.

Ammonium acetate solution has for a number of years been used by one of us in lecture demonstrations of buffer activity, for which purpose

it is very effective. Since the dissociation constants for ammonium hydroxide and acetic acid are often given in the literature as identical values, we decided to make an accurate determination of the P_H value of ammonium acetate solutions. Theoretically they should be neutral.

A quinhydrone electrode of the Cullen[1] type was used and a standard buffer solution (Arthur H. Thomas) 4.63 ± 0.01 P_H at 25°, was checked with it to the second decimal place. The following determinations were then made.

TABLE I

AMMONIUM ACETATE SOLUTION USED

	P_H value found
Approx. 0.5 *N* made with boiled distilled water	7.00
Approx. 0.1 *N* made with unboiled distilled water	7.01 7.01
Approx. 0.05 *N* made with unboiled distilled water	7.01
Approx. 0.5 *N* soln. (above) through which laboratory air had been bubbled for five minutes	6.95

From these results it is apparent that ammonium acetate solutions, through wide limits of concentration, are as nearly neutral as one could hope to get a solution, and are stable toward laboratory conditions. Since such a standard solution can be made in a moment's time there is no occasion, in any event, to store the solutions.

It may be pointed out that whereas buffered solutions, in general, change their P_H values only a little by dilution, the P_H value of a perfectly neutral buffer such as this one should not change at all on dilution.

The ammonium acetate solution above described is not only valuable as a standardizing solution for quinhydrone electrodes, etc., but may also be used as a standard in titrations when an exactly neutral end-point is desired. If one wishes to bring the color of his indicator exactly to the neutral point it is not necessary to guess at it. Indicator may be introduced into an ammonium acetate solution with assurance that it will assume a neutral tint which can be used for comparison.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON

RECEIVED JANUARY 18, 1932
PUBLISHED MAY 7, 1932

[1] Cullen, *J. Biol. Chem.*, **83**, 535 (1929).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATECHIN OF THE CACAO BEAN[1]

BY KARL FREUDENBERG,[1a] RICHARD F. B. COX[1a] AND EMIL BRAUN

RECEIVED JULY 16, 1931 PUBLISHED MAY 7, 1932

More than twenty years ago A. J. Ultée and W. van Dorssen detected in fresh cacao beans a phenolic crystalline substance which they called "Kakaool." They isolated it as a crystalline caffeine compound and suggested the formula $C_{16}H_{16}O_6$. The substance forms a crystalline acetyl compound with the melting point 153–154°.

From the description of this labile material, one of us concluded[2] that it belonged to the catechin class. When later the various isomeric forms of catechin became better known, the additional suggestion could be made that this substance very probably represented *l*-epicatechin.[3]

This prediction has now been proved to be correct. We prepared the catechin from a sample of fresh cacao pods procured from Trinidad (collected in January), and another procured from Porto Rico (collected in January). A third sample was kindly sent to us by Dr. A. Frey-Wyssling of Medan, Sumatra, and consisted of fresh beans sterilized in Medan. For the fourth sample we are indebted to Dr. A. J. Ultée, who supplied us with some of his original "caffeine-kakaool." From all these samples the same substance was obtained. It was identical in every respect with *l*-epicatechin, which was isolated some years ago from the wood of *Acacia Catechu*.[4]

While our present work was in progress, a paper by W. B. Adam, F. Hardy and M. Nierenstein[5] appeared in which the view was adopted that cacaol belongs to the catechin family. Their experimental results are in sufficient agreement with ours, and they identify it, as we do, with the levorotatory catechin present in the cutch-producing acacias; but they call it *l*-acacatechin and ascribe to it a constitutional formula which we believe is incorrect.

We maintain that catechin and epicatechin are stereoisomeric and that both have the formula I. The tetramethyl ether of each gives rise, after reduction and methylation, to the same pentamethoxy-1,3-diphenylpropane (II).[6] *dl*-Epicatechin has been obtained from cyanidin[7] by hydro-

[1] Researches on Tannins, No. 26; preceding communication, *Ann.*, **483**, 140 (1930).

[1a] Carl Schurz Memorial Professor for 1931 at the University of Wisconsin. Funds for the appointment of Mr. Cox were kindly furnished by a grant from the Wisconsin Alumni Research foundation.

[2] K. Freudenberg, *Ber.*, **53**, 1416 (1920).

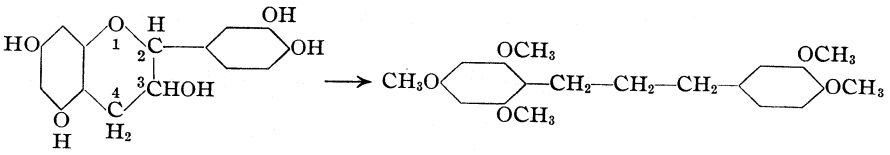
[3] K. Freudenberg and L. Oehler, *Ann.*, **483**, 141 (1930).

[4] Freudenberg, Fikentscher, Harder and Schmidt, *ibid.*, **444**, 139 (1925).

[5] Adam, Hardy and Nierenstein, THIS JOURNAL, **53**, 727 (1931).

[6] See *Ann.*, **451**, 213 (1926), Ref. 2 for references.

[7] Ref. 4, page 135.



I II

genation, and its pentamethyl ether from pentamethylcyanidin and pentamethylquercetin[8] in the same way. As the formulas of cyanidin and quercetin are definitely established, no doubt seems possible concerning the constitution of epicatechin.

Synthetic epicatechin is identical with a mixture of equal parts of natural *l*-epicatechin and *d*-epicatechin obtained by the epimerization of natural *d*-catechin.[9] *dl*-Epicatechin forms by epimerization *dl*-catechin[9] which is identical with a mixture of equal parts of natural *d*-catechin and *l*-catechin formed by the epimerization of *l*-epicatechin.[10] *dl*-Catechin in its turn can be converted into *dl*-epicatechin.[11] The scheme of these relationships given in 1924,[12] can be completed by an arrow leading from *dl*-epicatechin to *dl*-catechin. Catechin and epicatechin are, therefore, stereoisomers, and their constitution is expressed by the same formula (I). The fact that both yield the same 1,3-diphenylpropane derivative (II) leads to the same conclusion.

It has been deemed necessary to develop a part of the evidence given in favor of formula I for both catechin and epicatechin as M. Nierenstein[13] has been attempting for many years to establish another formula in which the catechol nucleus is attached to carbon atom 3 or 4 (I). He bases his suggestion on his failure to obtain substance II from either catechin or epicatechin.

As a matter of fact, M. Nierenstein has omitted to carry out, in accordance with our procedure,[6] this fundamental reaction leading from I to II, in spite of the various suggestions which have been made to him to perform this simple experiment.[14] We, therefore, confine ourselves to a few criticisms of some of his later papers.

[8] Freudenberg and Kammüller, *Ann.*, **451,** 209 (1927).

[9] Ref. 7, page 140.

[10] Freudenberg and Purrmann, *Ann.*, **437,** 283 (1924).

[11] Freudenberg, *Ber.*, **55,** 1738 (1922); Freudenberg and Purrmann, *ibid.*, **56,** 1190 (1923).

[12] See Ref. 10, page 275; Freudenberg and Harder, *Ann.*, **451,** 214, Ref. 3 (1927).

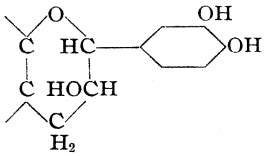
[13] Nierenstein, *Ber.*, **56,** 1877 (1923); THIS JOURNAL, **46,** 2793 (1924); *ibid.*, **48,** 1959 (1926); *ibid.*, **52,** 1672 (1930); *Chem. Age* (London), **19,** 291, 361 (1928); *J. Indian Chem. Soc.*, **7,** 279 (1930); for earlier quotations *cf. Ber.*, **56,** 2128, Ref. 5 (1923); *Ann.*, **437,** 279, Ref. 2 (1924); and the critical remarks, *Ber.*, **56,** 1188, Ref. 6 (1923); and *ibid.*, **55,** 1938 (1922).

[14] Nierenstein, *ibid.*, **56,** 1188, Ref. 6 (1923); *ibid.*, **55,** 1938 (1922); finally K. Freudenberg, some years ago, deposited authentic material in another laboratory and asked Dr. Nierenstein to write to this Laboratory for a part of this substance and carry out

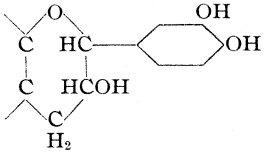
M. Nierenstein and E. O. Hazelton[15] tried to convert *dl*-catechin into *dl*-epicatechin and from their failure concluded that these substances cannot have the same structural formula. They overlooked the fact, mentioned above, that this conversion had been accomplished nine years before.

M. Nierenstein[16] is laboring under a misapprehension in assuming that the work of J. J. Drumm, R. J. P. Carolan and H. Ryan[17] proves a formula of catechin proposed by him and disproves our formula (I). The Irish authors, on the contrary, expressly state that their result is in agreement with our formula.[18]

Furthermore, M. Nierenstein[19] refers to a remark made by W. Hückel[20] as being a criticism of our formula. Some time ago[21] one of us suggested that, of the two stereoisomeric formulas derived from formula I, epicatechin has the spacial arrangement Ia and catechin Ib. Evidence for this de-



Ia



Ib

cision seemed to be given by the fact that tetramethylepicatechin readily loses water, while tetramethylcatechin splits off water only with difficulty, undergoing a rearrangement at the same time. Later[22] we again left open the question as to which formula of the two, Ia or Ib, must be ascribed to catechin or epicatechin. Two years later Hückel, who had overlooked the last remark, made the same suggestion. The criticism of Hückel was therefore unnecessary, and did not touch at all upon the question of constitution as might be inferred from Nierenstein's remark.

We state once more that all catechins which K. Freudenberg and his collaborators have had in hand thus far, are stereoisomeric catechins or epicatechins and are all to be expressed by formula I.

Experimental

The beans used in this investigation were heated for an hour at 75° in 95% alcohol, immediately after removal from the pods, in order to kill enzymes. After air-drying

the experiment. *Cf.* R. Robinson's remarks on the question [*Chem. Age* (London), **19,** 337 (1928)].

[15] Nierenstein and Hazelton, *J. Indian Chem. Soc.*, **7,** 279 (1930).

[16] Nierenstein, THIS JOURNAL, **53,** 1500 (1931).

[17] Drumm, Carolan and Ryan, *Proc. Royal Irish Acad.*, [B] **39,** 114 (1929).

[18] *Cf.* R. Robinson, *Chem. Age* (London), 19 (1928).

[19] Ref. 16, page 1501.

[20] Hückel, *Ann.*, **477,** 159 (1929).

[21] Freudenberg, Fikentscher and Wenner, *Ann.*, **442,** 309 (1925); Freudenberg, Carrara and Cohn, *ibid.*, **446,** 87 (1925).

[22] Freudenberg and Harder, *ibid.*, **451,** 214 (1927).

they were ground in a mill and the catechin removed by maceration with alcohol at 75°. The alcohol solution contained fat, caffein and catechin. After removal of the alcohol under reduced pressure, the residue, dissolved in a little water, was extracted a few times with petroleum ether for removal of fat, and then exhaustively extracted with chloroform to remove the caffein. The resulting deep red solution was extracted with ether for several days. The solid remaining after evaporation of the ether was taken up in a small quantity of boiling water, treated with talcum to absorb any fat that might be present, and allowed to crystallize. After several days, small rosets of thick prisms had crystallized from the solution. These were of a slight brownish-pink tinge and had to be purified from an acetone–benzene solution.[23]

The material obtained from Trinidad and Porto Rico was sterilized after arrival in Madison, whereas the beans from Sumatra were sterilized there. The meat of the latter beans was light pink, while the meat of the former two samples was dark brown. The yield obtained from the first two samples was only one to two-tenths while the yield from the Sumatra beans was five-tenths of one per cent.

Two and three-tenths grams of the compound sent by Dr. Ultée was dissolved in 25 cc. of hot water, filtered to remove solid impurities and extracted fifteen times in a separatory funnel with 15-cc. portions of chloroform. The water layer was then heated to boiling, filtered and set aside to crystallize. It was seeded with *l*-epicatechin, and the next day a crop of crystals was obtained.

The crystalline form and solubilities of the four samples did not differ from those of *l*-epicatechin. The crystals lost four molecules of water at 100° under reduced pressure (av. 19.5%, calcd. 19.9%).[24] The water of crystallization is lost slowly at room temperature.

When heated, following the procedure of E. Fischer,[25] the substances decomposed at 237–239° (corr. 245°). *l*-Epicatechin itself and mixtures of the substances with *l*-epicatechin behaved likewise.[26]

The rotation of the catechin of cacao was measured in acetone–water (1:1 by weight): $[\alpha]_D^{20}$ $-0.58 \times 100/1 \times 0.998 = -58°$. For *l*-epicatechin in yellow mercury light, −59–60° is indicated.[27] (M. Nierenstein[5] used water and found −69°.)

Anal. Subs., 4.368 mg.: CO_2, 9.98; H_2O, 1.99. Calcd. for *l*-epicatechin: C, 62.07; H, 4.82. Found: C, 62.31; H, 5.09.

The acetyl compound was prepared in the usual way.[28] The melting point of pentacetyl-*l*-epicatechin was 151–152° (corr. 153–154°).[29] When mixed with the original preparation the melting point did not alter.

The acetates of our cacao-catechin as well as the acetate of Dr. Ultée's material had the same rotation in acetylene tetrachloride, varying from −12.1 to −12.3°; $[\alpha]_D^{20}$ $-1.09 \times 100/1 \times 8.84 = -12.3$.

Anal. Subs., 4.332 mg.: CO_2, 9.51; H_2O, 1.87. Calcd. for pentacetyl-*l*-epicatechin: C, 59.98; H, 4.83. Found: C, 59.87; H, 4.83.

---

[23] Ref. 4, page 144.

[24] Ref. 10, page 276.

[25] Fischer, *Ber.*, **41**, 75 (1908).

[26] The point of decomposition of 245° as indicated in *Ann.*, **437**, 276 (1924), is corrected (*cf. Ber.*, **56**, 1192 (1923)). M. Nierenstein (ref. 5) indicated a melting point of 229°. When heated slowly, this point of decomposition can also be obtained with our substances.

[27] Freudenberg and Purrmann, (a) *Ann.*, **437**, 276 (1924); (b) *Ber.*, **56**, 1192 (1923).

[28] Freudenberg, Böhme and Beckendorf, *ibid.*, **54**, 1209 (1921).

[29] Freudenberg and Purrmann, *ibid.*, **56**, 1189 (1923); *Ann.*, **437**, 276 (1924).

In a 2–3% solution with mercury light, specific rotations of −14.5 to −15.0° were found for *l*-epicatechin pentacetate. M. Nierenstein reports −12° for sodium light (concentration not indicated).

The melting points reported by M. Nierenstein and his collaborators[30] for the acetates of the so-called *dl*-acacatechin (160°), *d*-gambircatechin (137°), *dl*-gambircatechin (156°) do not correspond to those for our pure substances. The acetates of *dl*-epicatechin, *d*-catechin and *dl*-catechin melt at 169°, 131–132°, 164–165°, respectively.[28a]

Summary

1. The catechin present in the cacao bean is shown to be identical with *l*-epicatechin.

2. Recent work of Dr. Nierenstein is criticized.

[30] Ref. 5, p. 1504.

MADISON, WISCONSIN, AND HEIDELBERG, GERMANY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF THE OZARKS]

THE PREPARATION OF 5,7-DI-IODOISATIN

BY WARD C. SUMPTER AND LAWRENCE AMUNDSEN

RECEIVED OCTOBER 19, 1931 PUBLISHED MAY 7, 1932

The preparation of 5,7-di-iodoisatin has been described by Kalb and Berrer.[1] These investigators treated an aqueous solution of the sodium bisulfite addition compound of dehydroindigo with iodine monochloride. 5,7-Di-iodoisatin was obtained by treating the resulting solution with a solution of potassium dichromate in aqueous sulfuric acid.

The writers attempted to repeat the work of Kalb and Berrer but were able to obtain only very poor yields of the compound by this method. A procedure was then developed for preparing 5,7-di-iodoisatin from 5,7,5′,7′-tetraiodoindigo. The latter compound was oxidized with an aqueous solution of chromic and nitric acids and more satisfactory yields of the di-iodoisatin were obtained.

It has also been stated that 5,7-di-iodoisatin,[2] as well as a small amount of tetraiodoisatin, is obtained when a solution of isatin in concentrated hydrochloric acid is treated with iodine monochloride. Hill and Sumpter found that this statement[3] is in error, 5-iodoisatin being the sole product even when a large excess of iodine monochloride is used.

The writers have further attempted to prepare 5,7-di-iodoisatin by the action of iodine monochloride on isatin and on iodoisatin in methyl alcohol, ethyl alcohol, concentrated sulfuric acid, fuming sulfuric acid and acetic anhydride without success. It appears that iodine cannot be introduced

[1] Kalb and Berrer, *Ber.*, **57**, 2112 (1924).

[2] German Patent 429,101.

[3] Sumpter, Ph.D. Dissertation, Yale University, 1930.

directly into the isatin nucleus in position 7. This is in keeping with the observations of Borsche[4] and of Kalb and Berrer,[1] who also reported that 5,7-di-iodoisatin could not be obtained by the iodination of isatin.

Experimental Part

5,7,5′,7′-Tetraiodoindigo.—This compound was prepared according to the directions given by Kalb and Berrer.[5] The yields averaged 60% of the theoretical.

5,7-Di-iodoisatin. A. By the Method of Kalb and Berrer.[1]—Repeated experiments using 10 g. of the sodium bisulfite addition compound gave yields of 1.7–1.8 g. or about 10% of the theoretical. Kalb and Berrer reported 48% yields.

B. By the Oxidation of Tetraiodoindigo.—Ten grams of tetraiodoindigo was suspended in 20 cc. of water and the mixture heated to boiling. A solution of 8.4 g. of chromic acid in 35 cc. of concentrated nitric acid was slowly added to the mixture and the boiling continued for ten minutes; 100 cc. of water was added to the mixture and the insoluble material filtered off. The residue was digested with 150 cc. of hot 10% sodium hydroxide, the whole diluted to a volume of 1500 cc. by the addition of water, boiled for ten minutes and filtered into an excess of dilute hydrochloric acid. The precipitate of 5,7-di-iodoisatin was filtered off and purified by crystallization from glacial acetic acid. It separated in characteristic red plates, m. p. 261–263°. Kalb and Berrer reported decomposition at 240°. The compound is identical with that which was obtained in poorer yields by the procedure of Kalb and Berrer. The yield was 6.3 g. or 60% of the theoretical.

Anal. Calcd. for $C_8H_3O_2NI_2$: N, 3.50; I, 63.66. Found: N, 3.50, 3.46; I, 62.85.

Oxidation of the di-iodoisatin with 3% hydrogen peroxide in alkaline solution gave 2-amino-3,5-di-iodobenzoic acid (m. p. 230°) as stated by Kalb and Berrer.

Summary

5,7-Di-iodoisatin has been prepared by the action of chromic and nitric acids on 5,7,5′,7′-tetraiodoindigo.

CLARKSVILLE, ARKANSAS

[4] Borsche, Weussman and Fritzsche, *Ber.*, **57**, 1770–1775 (1924).

[5] Kalb and Berrer, *ibid.*, **57**, 2105 (1924).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 78]

CONDENSATION BY SODIUM INSTEAD OF BY THE GRIGNARD REACTION. IV. THE PROBABLE EXISTENCE OF A NEW INTERMEDIATE, "METAL HALYL," IN THE REACTION

BY AVERY A. MORTON AND JOSEPH R. STEVENS

RECEIVED NOVEMBER 6, 1931 PUBLISHED MAY 7, 1932

The action of an alkali metal on a halogenated hydrocarbon has commonly been explained by assuming the intermediate formation of either a metal alkyl or aryl,[1] or a free hydrocarbon radical.[1e,2] The idea of an earlier stage in which the metal is attached to the organic halide in a complex has received scant attention.[3] Having made a study on this point we shall present herein experiments for which a reasonable interpretation lies in the assumption of such an intermediate compound. As examples we have observed the behavior of sodium with chlorobenzene, bromobenzene, and butyl chloride. The complexes assumed to occur may be designated as chlorobenzene sodium,[4] bromobenzene sodium, and butyl chloride sodium, respectively. Because of certain analogies with the metal ketyls, to be pointed out in the following paragraphs, we shall consider these complexes as belonging to a new class of compounds to be called "Metal halyls."

Evidence for the above is found in the action of sodium on triphenylchloromethane carried out, on the one hand, in the presence of benzophenone or tetraphenylethylene and, on the other, in the presence of chloro- or of bromobenzene. When sodium is allowed to stand with triphenylchloromethane in benzene or ether solution no reaction occurs, but if benzophenone is added, the sodium first combines with the ketone, as shown by the color change, forming the metal ketyl, which in turn reacts with triphenylchloromethane to produce triphenylmethyl, sodium chloride and benzophenone. In other words, the benzophenone has acted as a carrier of sodium to triphenylchloromethane. A similar result is obtained

[1] For example see (a) Acree, *Am. Chem. J.*, **29**, 588 (1903); (b) Schorigin, *Ber.*, **41**, 2717 (1908); (c) Goldschmidt and Schön, *ibid.*, **59**, 948 (1926); (d) Ziegler and Colonius, *Ann.*, **479**, 135 (1930); (e) Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

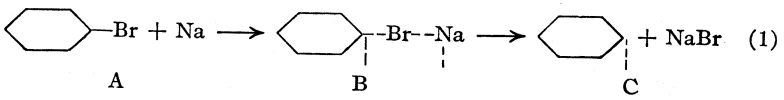
[2] For example see (a) Marvel, Hager and Coffman, THIS JOURNAL, **49**, 2323 (1927); (b) Bachmann and Clarke, *ibid.*, **49**, 2089 (1927).

[3] The formation of the blue color in the Wurtz–Fittig reaction has received considerable attention from investigators. Among others Krafft and Göttig, *Ber.*, **21**, 3187 (1888), discuss the formation of a complex. Schlubach and Goes[1e] find no evidence for organic matter in the blue compound. Wooster, THIS JOURNAL, **51**, 1856 (1929), interprets certain statements by Schmidlin in "Das Triphenylmethyl" as referring to the formula C_2H_5NaBr. Staudinger, *Z. Elektrochem.*, **31**, 549 (1925), has advanced the idea of a "Mol-Halogenide" as an intermediate product to account for the explosive nature of mixtures of alkali metals and certain halides.

[4] In naming the organic metal compounds we have adopted the recent practice of putting the metal last.

when tetraphenylethylene is substituted for benzophenone. The sodium first adds to the ethylenic linkage from which position it reacts with triphenylchloromethane forming triphenylmethyl, and regenerating tetraphenylethylene. It is clear that the initial step in each of these cases has been the addition of sodium to a polar atom, after which the metal is able to act upon the triarylchloromethane.

Chloro- or bromobenzene acts similarly to benzophenone or tetraphenylethylene in causing sodium to attack triphenylchloromethane.[5] We can assume, therefore, that sodium first attaches itself to the polar atom in chlorobenzene, forming a "Sodium Halyl," but before sufficient time has elapsed to remove completely the halogen from the phenyl radical, as in a Fittig synthesis, the complex meets a molecule of triphenylchloromethane and reacts with the latter forming triphenylmethyl. The only difference between benzophenone and tetraphenylethylene on the one hand, and chloro- or bromobenzene on the other, is that the former substances have no atoms which can be removed readily by sodium, whereas the latter will, if given time, lose their halogens completely to the alkali metal. Let us express the action of sodium on bromobenzene as in equation (1). "B" illustrates the complex designated as a "Sodium halyl." The dotted lines

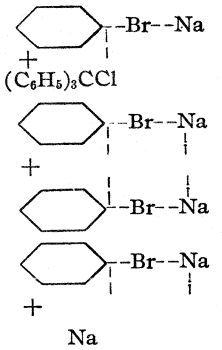


(1)

represent partial valences, some of which serve to bind the phenyl radical and the sodium to the polar atom, bromine, and others are unsaturated, representing unused combining power.[6] These free partial valences enable the complex to react either with a molecule of triphenylchloromethane forming triphenylmethyl, equation (2); or with another complex of the same kind forming diphenyl, equation (3); or with an atom of sodium forming phenylsodium, equation (4). If left to itself the complex will eventually form the free radical, phenyl, and sodium bromide as shown in stage C, equation (1).

[5] We wish to acknowledge our indebtedness to Professor Norris for calling to our attention the fact that Norris and Sanders, *Am. Chem. J.*, **25**, 58 (1901), observed the formation of triphenylmethyl from triphenylchloromethane and bromobenzene in the presence of sodium. This fact has been the basis for the experiments described in this paper.

[6] We recognize that it is possible to picture the complex by an associated molecule, a quinoid compound, or some electronic idea. One might also think of the complex as in a dormant state, awaiting the acquisition of sufficient energy to change to the state C; or as in a continual state of change due to the pulling action of the phenyl radical and the sodium atom for the bromine, as if in a tug of war. These interesting speculations are beyond the scope of this paper. We have adopted a form of writing this complex which expresses in the simplest manner possible the reactions and resemblances to the metal ketyls.



$$\longrightarrow (C_6H_5)_3C + C_6H_5Br + NaCl \quad (2)$$

$$\longrightarrow C_6H_5C_6H_5 + 2NaBr \quad (3)$$

$$\longrightarrow C_6H_5Na + NaBr \quad (4)$$

If such a picture of the role of the halide as a carrier of sodium is correct, the chloro- or bromobenzene should be recovered at the end practically unchanged. We have been able to test this hypothesis quantitatively by comparing the amounts of sodium chloride and bromide formed in the reaction of sodium on triphenylchloromethane in the presence of bromobenzene. If the reaction proceeds by the intermediate formation of the "Sodium halyl" which later gives up its sodium as shown in equation (5), sodium chloride will be formed exclusively. If, on the other hand,

$$\begin{aligned} C_6H_5Br + Na &\longrightarrow C_6H_5BrNa \\ C_6H_5BrNa + (C_6H_5)_3CCl &\longrightarrow (C_6H_5)_3C + NaCl + C_6H_5Br \end{aligned} \quad (5)$$

the reaction occurs through the formation of phenylsodium as shown in equation (6), sodium chloride and sodium bromide must be formed in equivalent quantities. Ideal conditions, naturally, will never exist as some

$$\begin{aligned} C_6H_5Br + 2Na &\longrightarrow C_6H_5Na + NaBr \\ C_6H_5Na + (C_6H_5)_3CCl &\longrightarrow (C_6H_5)_3C + {}^1/_2C_6H_5C_6H_5 + NaCl \end{aligned} \quad (6)$$

sodium bromide will result from a Fittig reaction. As we increase the concentration of triphenylchloromethane, however, the ratio of chloride to bromide formed will approach 100% sodium chloride if the "Sodium halyl" is the intermediate, and will approach only 50% sodium chloride if phenylsodium is the agent. It is apparent from the analyses of the halides (see Fig. 1), that the quantity of sodium chloride is well above the 50% line demanded by equation (6) and under favorable conditions reaches nearly 88% of the total halides formed. This result shows conclusively that the two are not formed in equivalent quantities and suggests that the probable[7] course is through the formation of a "Sodium halyl."

[7] It is still possible, of course, to write the changes using a free phenyl radical as an intermediate. Thus

$$\begin{aligned} C_6H_5Br + Na &\longrightarrow C_6H_5 + NaBr \\ C_6H_5 + Na &\longrightarrow C_6H_5Na \\ C_6H_5Na + (C_6H_5)_3CCl &\longrightarrow (C_6H_5)_3C + C_6H_5 + NaCl \\ C_6H_5 + Na &\longrightarrow C_6H_5Na, \text{ etc.} \end{aligned}$$

However, it is exceedingly unlikely that a free phenyl radical would continue such a role

Application of these ideas to some of the reactions which we have discussed in previous papers[8] of this series may be made as in equations (7).

$$\begin{array}{l} C_6H_5ClNa \\ + \\ (C_6H_5)_2CONa \end{array} \longrightarrow (C_6H_5)_3CONa + NaCl$$

$$\begin{array}{l} C_2H_5BrNa \\ + \\ C_6H_5\overset{H}{\underset{|}{C}}ONa \end{array} \longrightarrow \begin{array}{l} C_2H_5 \\ C_6H_5 \end{array}\!\!>\!\overset{H}{\underset{|}{C}}ONa + NaBr \qquad (7)$$

In drawing conclusions as to the mechanism of reactions in which sodium is involved, it will be necessary in the future to distinguish more closely between the various possibilities. It is reasonable to consider that all three, *viz.*, the "Metal halyl," the metal alkyl or aryl, and the free radical may, on superficial examination, appear to bring about identical reactions. We have shown, as a matter of fact, that phenylsodium, prepared separately, will cause the formation of triphenylmethyl from triphenylchloromethane and it is very likely that a free phenyl radical, if it could be isolated as such, would also form triphenylmethyl. Further studies are being made.

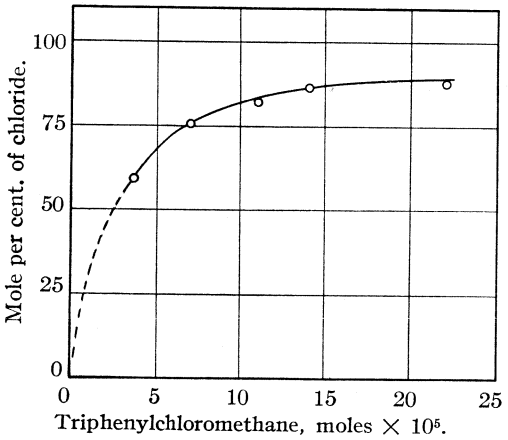


Fig. 1.

Experiments

The Action of Sodium on Triphenylchloromethane in the Presence of Benzophenone.—Triphenylchloromethane, 2 g., and benzophenone, 1 g., dissolved in 25 cc. of anhydrous ether were put into a closed tube with a small lump of sodium. The surface of the sodium became coated with the blue color of benzophenone ketyl but the solution was yellow from the formation of triphenylmethyl. When air was admitted triphenylmethyl peroxide precipitated. It was identified by means of a mixed melting point. When a similar reaction mixture was allowed to stand for three days it went through the stages of formation of benzophenone sodium ketyl which was blue on the surface of the sodium, triphenylmethyl which was yellow in solution, triphenylmethyl sodium as the solution became red, and finally the blue of benzophenone sodium in solution. All of these changes were clearly evident. After treating the reaction mixture with water

as a carrier of sodium when it could even more readily react with triphenylchloromethane and with itself.

[8] THIS JOURNAL, **53**, 2244, 2769, 4028 (1931).

and evaporating the ether, the residue was dissolved in benzene and shaken with concentrated sulfuric acid several times to remove all of the peroxide and carbinol present. A mixture of hydrocarbons was obtained from the benzene layer. This mixture was washed twice with hot acetone to remove any triphenylmethane present. The mixture melted up to 185°. The amount present was very small but it is possible that some hydrocarbon was formed other than triphenylmethane and *p*-benzhydryltetraphenylmethane.

The observation of Schlenk and co-workers,[9] that benzophenone sodium added to triphenylchloromethane should cause the formation of triphenylmethyl, was confirmed. The blue color of the ketyl was instantly discharged and the yellow color of triphenylmethyl appeared. From the mixture the peroxide was precipitated when air was admitted.

The Action of Sodium on Triphenylchloromethane in the Presence of Tetraphenylethylene.—To a solution of 0.25 g. of triphenylchloromethane in 10 cc. of ether in contact with 0.25 g. of sodium was added 0.25 g. of tetraphenylethylene.[10] The solution became yellow, indicating the formation of triphenylmethyl. When air was admitted triphenylmethyl peroxide was precipitated. It was identified by a melting point and a mixed melting point.

The Action of Sodium on Triphenylchloromethane in the Presence of Chlorobenzene, Bromobenzene or Butyl Chloride.—To a solution of triphenylchloromethane, 0.2 g. in 20 cc. of anhydrous benzene in contact with 1 g. of sodium, was added 5 g. of chlorobenzene. The yellow color of triphenylmethyl formed easily. When air was let into the tube triphenylmethyl peroxide precipitated. Similar experiments with bromobenzene and with *n*-butyl chloride gave the same results. A blank experiment of triphenylchloromethane with sodium in benzene showed that no triphenylmethyl had formed after the mixture had stood for sixty days.

The Action of Phenylsodium on Triphenylchloromethane.—Two grams of triphenylchloromethane in benzene was added to a suspension of phenylsodium in benzene, made from 2 g. of diphenyl mercury and an excess of sodium wire. Heat was evolved and a strongly colored solution of triphenylmethyl was formed. When air was admitted the peroxide precipitated and was identified by means of a mixed melting point. On evaporation of the mother liquors a small amount of a gummy material remained in which no evidence of tetraphenylmethane could be found. Our original purpose in this experiment was to observe if a different product was formed when the metal aryl was an intermediate in the reaction. The failure to find tetraphenylmethane led to an investigation of the relative quantities of chloride and bromide formed when triphenylchloromethane reacts with sodium in the presence of bromobenzene.

The Determination of the Amount of Sodium Bromide and Sodium Chloride Formed in Mixtures of Triphenylchloromethane and Bromobenzene.—A number of experiments were made in which mixtures of triphenylchloromethane and bromobenzene in 10 cc. of benzene were allowed to stand in contact with very nearly enough sodium to combine completely with all of the bromine in bromobenzene. The quantity of triphenylchloromethane was varied. When the sodium had disappeared the tube was opened and the solid material filtered. After washing the solid twice with considerable anhydrous warm benzene to remove any triphenylchloromethane present, it was washed with anhydrous petroleum ether and dried. The halides were then dissolved in water and filtered through the same filter to remove the small quantity of organic insoluble material which was present. After acidification with nitric acid, a portion of the filtrate

[9] Schlenk and Thal, *Ber.*, **46**, 2854 (1913); Schlenk and Ochs, *ibid.*, **49**, 612 (1916).

[10] Schlenk and Mark [*ibid.*, **55**, 2289 (1922)] added tetraphenylethylene sodium to triphenylchloromethane forming triphenylmethyl.

was treated with an excess of standard silver nitrate solution. The mixture of silver halides was filtered, washed, and weighed. The excess of silver nitrate was titrated with potassium thiocyanate solution using ferric alum as an indicator. From the volumetric results the number of moles of silver halides precipitated could be determined, which value, with the grams of silver halides from the gravimetric analysis of the same sample, enabled one to calculate the moles of chloride and of bromide present. Table I summarizes the results of these calculations.

TABLE I

GRAM ATOMS OF SODIUM, 0.004; MOLES OF BROMOBENZENE, 0.0048; CC. OF BENZENE, 10

Triphenylchloromethane, mole	Silver nitrate equivalent to silver halide precipitated, cc. of 0.0918 *N* solution	Silver halide, grams	Moles of bromide $\times 10^5$	Moles of chloride $\times 10^5$	Mole per cent. of chloride
0.0036	19.93	0.2951	74.2	108.8	59.4
.007	20.74	.2935	45.5	144.9	76.0
.011	24.38	.3392	40.3	183.5	82.1
.014	23.09	.3166	29.0	183.0	86.3
.022	20.76	.2836	23.2	167.4	87.9

In order to make sure that triphenylchloromethane did not react with the sodium bromide formed during the reaction, a blank test was made by allowing a mixture of 0.0061 mole of triphenylchloromethane to remain in contact with 0.009 mole of sodium bromide under conditions comparable to those in which the action of sodium has been observed. From this mixture the halides obtained by the method given above were found in two separate determinations to be 99.8 and 100.6% sodium bromide.

Conclusions

Chlorobenzene, bromobenzene and butyl chloride have been shown to act as carriers of sodium to triphenylchloromethane, in which respect they are similar to benzophenone and tetraphenylethylene.

Analyses of the halides formed in the reaction of sodium with triphenylchloromethane in the presence of bromobenzene shows that sodium chloride is formed to a greater extent than sodium bromide.

The above facts are interpreted as indicating the formation of a complex between sodium and bromobenzene. Complexes of this type are designated as "Metal halyls" because of their similarity to metal ketyls.

The position of the "Metal halyl" as an intermediate first step in the formation of a free hydrocarbon radical and metal alkyls or aryls is discussed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, LOYOLA UNIVERSITY, SCHOOL OF MEDICINE]

THREE NEW DERIVATIVES OF *d*-GLUCOHEPTULOSE[1]

BY W. C. AUSTIN

RECEIVED NOVEMBER 9, 1931 PUBLISHED MAY 7, 1932

In 1930 the writer,[2] in association with Hudson, described the preparation of a new crystalline ketoheptose, *d*-glucoheptulose, from *d*-α-glucoheptose following rearrangement of the latter with dilute alkali. The *d*-glucoheptulose was reported to have a rotation of $[\alpha]_D^{20}$ +67.5°, without mutarotation. In order to determine whether the *d*-glucoheptulose exists in the alpha or beta form it became necessary to prepare the methyl-*d*-glucoheptuloside from it. By heating *d*-glucoheptulose in methyl alcohol containing 1% of dry hydrogen chloride there was formed the crystalline α-methyl-*d*-glucoheptuloside, of $[\alpha]_D^{20-25}$ +108.5° in water, melting at 138–140°. It will be shown later in this article that the rotation of this derivative proves that the *d*-glucoheptulose exists in the alpha form.

By acetylating the α-methyl-*d*-glucoheptuloside with acetic anhydride and sodium acetate, the α-methyl-*d*-glucoheptuloside pentaacetate has been prepared in crystalline form. This second new derivative of *d*-glucoheptulose has been recrystallized to constant specific rotation, $[\alpha]_D^{20-25}$ +78.5°, in chloroform, with m. p. 110°.

The acetylation of *d*-glucoheptulose with acetic anhydride and sodium acetate has given the crystalline *d*-glucoheptulose α-hexaacetate, which has been purified to constant specific rotation, $[\alpha]_D^{20-25}$ +87.0°, in chloroform, with m. p. 112°.

Calculation of the Rotations of the Beta Forms of the above Derivatives of *d*-Glucoheptulose.—The rotations of the above alpha forms of the three derivatives of *d*-glucoheptulose will now be examined in connection with those of α-methyl-*d*-fructoside and its tetraacetate, recently described by Schlubach and Schröter.[3] These workers have called attention to the fact that the values of the rotations of the end asymmetric carbon atoms may now be calculated for these derivatives of *d*-fructose by the application of the rule of Hudson,[4] taking one-half the difference between the molecular rotations of the alpha and beta isomers. The β-methyl-*d*-fructoside and its tetraacetate, beta isomers of the two alpha compounds recently prepared by Schlubach and Schröter, were made in 1916 by Hudson and Brauns.[5a] The alpha and beta forms of *d*-fructose penta-

[1] Announced, in part, on the program of the meeting of the American Chemical Society in Minneapolis, Minn., Sept. 9–13, 1929. The author desires to thank Mr. B. J. Gregory for valuable technical assistance.

[2] Austin, THIS JOURNAL, **52**, 2106 (1930).

[3] Schlubach and Schröter, *Ber.*, **61**, 1216 (1928); **63**, 363 (1930).

[4] Hudson, THIS JOURNAL, **31**, 66 (1909).

[5] (a) Hudson and Brauns, *ibid.*, **38**, 1216 (1916); (b) **37**, 1283, 2736 (1915).

acetate were also prepared by Hudson and Brauns[5b] and furnish values of rotations for determining the value of the end asymmetric carbon atom in the *d*-fructose pentaacetate. The determinations on the three pairs of isomers are shown in Table I for these fructose derivatives. For purposes of comparison the corresponding values given by Hudson[6] for the aldoses are also given in the tabulation.

TABLE I

VALUES OF THE COEFFICIENT a_{Me}, A_{Me} AND A_{Ac} IN THE FRUCTOSE SERIES

Substance	Mol. wt.	$[\alpha]_D^{20}$ in water	$[M]_D$	Rotation of end Carbon, A	A for corresponding derivatives of aldoses
α-Methyl-*d*-fructoside	194	+ 46.0°	+ 8,900	a_{Me} = 21,200	a_{Me} = 18,700
β-Methyl-*d*-fructoside	194	−172.7°	−33,500		
Tetraacetates of		$[\alpha]_D^{20}$, in $CHCl_3$			
α-Methyl-*d*-fructoside	362	+ 45.5°	+16,850	A_{Me} = 31,050	A_{Me} = 26,900
β-Methyl-*d*-fructoside	362	−125.0°	−45,250		
Pentaacetates of					
α-*d*-Fructose	390	+ 34.7°	+13,533	A_{Ac} = 30,458	A_{Ac} = 19,100
β-*d*-Fructose	390	−121.5°	−47,384		

Schlubach and Schröter have called attention to the fact that the values of a_{Me} and A_{Me} are greater for the derivatives of fructose than for the corresponding derivatives of aldoses. Differences of the same nature are observed in comparison of the value A_{Ac} from derivatives of fructose with that from derivatives of aldoses. The reason for these differences between the corresponding coefficients of fructose and the aldoses is not definitely known. The differences may be due to the fact that the end asymmetric carbon atom in fructose is attached to —CH_2OH or to —CH_2OR instead of to —H, as in the aldoses and their derivatives. The attachment of additional weight to the end asymmetric carbon in the fructose series may cause its rotation to be larger than in the aldose series; this explanation would lead one to expect that the rotation coefficients of the fructose series will be found to apply in other 2-ketose series. For the present it is assumed that the values of a_{Me}, A_{Me} and A_{Ac} are the same in the fructose and glucoheptulose series on account of the like groups attached to carbon 2 in these ketoses.[7] The values of the rotations of the unknown beta isomers of the three known alpha derivatives of *d*-glucoheptulose may now be calculated by deducting from the molecular rotation of the alpha isomer twice the value of the rotation of the end asymmetric carbon atom for the corresponding derivative of fructose and dividing the difference so obtained by the molecular weight of the beta isomer.

The value of the $[M]_D$ of α-methyl-*d*-glucoheptuloside is (+108.5°)

[6] Hudson, THIS JOURNAL, **48**, 1428 (1926).

[7] I am indebted to Dr. C. S. Hudson for the suggestion that the coefficients of the fructose series may apply to the series of the 2-ketose sugars in general.

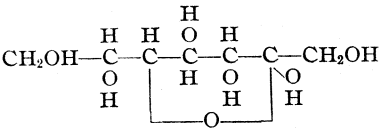
(224) = +24,300. The value of $2a_{Me}$ from the fructose series is +42,400, and the difference is −18,100, which is the calculated $[M]_D$ for β-methyl-*d*-glucoheptuloside. The corresponding specific rotation is $[\alpha]_D$ = −18,100/224 = −81.0°.

The value of the $[M]_D$ of α-methyl-*d*-glucoheptuloside pentaacetate is (+78.5°) (434) = +34,069. The value of $2A_{Me}$ from the fructose series is +62,100, and the difference is −28,031, which is the calculated $[M]_D$ for β-methyl-*d*-glucoheptuloside pentaacetate. The corresponding specific rotation is $[\alpha]_D$ = −28,031/434 = −64.6°.

The value of the $[M]_D$ of *d*-glucoheptulose α-hexaacetate is (+87.5°) (462) = +40,424. The value of $2A_{Ac}$ from the fructose series is +60,917, and the difference is −20,493, which is the calculated $[M]_D$ for *d*-glucoheptulose β-hexaacetate. The corresponding specific rotation is −20,493/-462 = −44.3°.

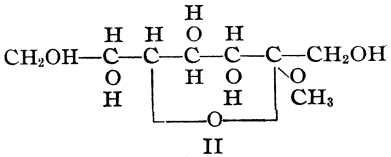
On page 1928 the rotation of the unknown beta form of *d*-glucoheptulose is calculated by a slightly different method.

The Ring Structure of the Derivatives of *d*-Glucoheptulose.—In the article describing the preparation of *d*-glucoheptulose, shown as structure I, evidence was given that the new sugar contained the 2,5 ring. Proof may now be advanced that the ring structure of the derivatives of *d*-glucoheptulose is also 2,5, and that the structures of the new derivatives are those represented in II, III and IV.



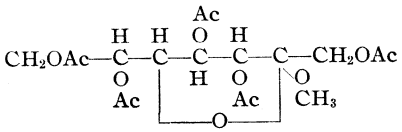
I

d-Glucoheptulose(2,5)



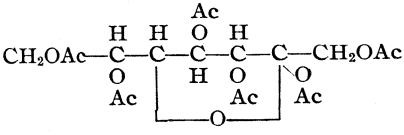
II

α-Methyl-*d*-glucoheptuloside(2,5)



III

α-Methyl-*d*-glucoheptuloside pentaacetate(2,5)



IV

d-Glucoheptulose α-hexaacetate(2,5)

In each of the structures shown the asymmetric carbon atoms (Nos. 3, 4, 5 and 6) have the same configurations as the corresponding asymmetric carbon atoms (Nos. 2, 3, 4 and 5) of *d*-glucose, or the corresponding derivative of this sugar with the 1,4 ring. The rotations of *d*-glucose and its derivatives with this ring have not been measured because the substances are not known, but the values of the rotations have been calculated by Hudson.[8] Using the values for the corresponding derivatives of *d*-glucose-

[8] Hudson, THIS JOURNAL, **48**, 1434 (1926); **52**, 1680 (1930).

(1,4) it should be possible to calculate the rotations of the derivatives of *d*-glucoheptulose, with the same type of ring(2,5).

Hudson has calculated for the α-methyl-*d*-glucoside(1,4) the rotation $[\alpha]_D$ +114°, or $[M]_D$ (+114°) (194) = +22,120. By subtracting from the $[M]_D$ of this compound the value of a_{Me} for aldoses, +18,700, there is obtained the value of $B_{d\text{-glucose}(1,4)}$ = +3420. The $[M]_D$ for α-methyl-*d*-glucoheptuloside(2,5) should be the value $B_{d\text{-glucose}(1,4)}$ plus a_{Me} from the fructose series, +21,200, giving +24,620. The corresponding $[\alpha]_D$ value is +24,620/224 = +110°. This calculated value is so near the observed value of +108.5° that it may be safely concluded that the α-methyl-*d*-glucoheptuloside is an alpha form and has the 2,5 ring.

Haworth and Porter[9] have prepared α-ethyl-*d*-glucoside(1,4) and β-ethyl-*d*-glucoside(1,4), with $[\alpha]_D$ values of +98 and −86°, respectively. By taking one-half the sum of the values of the $[M]_D$ of these compounds, +20,384 and −17,888, the value of $B_{d\text{-glucose}(1,4)}$ is obtained = +1248. The $[M]_D$ of α-methyl-*d*-glucoheptuloside(2,5) should be the value of $B_{d\text{-glucose}(1,4)}$ plus a_{Me} from the fructose series, +21,200, giving +22,448, which corresponds to the $[\alpha]_D$ value of +100°. By subtracting from the value of $B_{d\text{-glucose}(1,4)}$ the value of a_{Me} from the fructose series the $[M]_D$ of β-methyl-*d*-glucoheptuloside(2,5) is found to be −19,952, corresponding to the $[\alpha]_D$ value of −89°. The differences of 8° between the values calculated by this method and the values found for the α-methyl-*d*-glucoheptuloside(2,5), or calculated for the β-methyl-*d*-glucoheptuloside-(2,5) by the method on page 1926, are not in conflict with the conclusions from the calculations in the preceding paragraph and are due to the slight differences in the values of $B_{d\text{-glucose}(1,4)}$ as calculated from the data of Hudson or from the observations of Haworth and Porter.

The specific rotation of the α-methyl-*d*-glucoheptuloside pentaacetate-(2,5) may be calculated similarly. The $[M]_D$ of the corresponding compound of *d*-glucose(1,4) is (+83°) (362) = +30,046. From this value of +30,046 the value of A_{Me} for aldoses, +26,900, is subtracted to give the value $B_{d\text{-glucose}(1,4),\ Ac}$ = +3146. By adding the value of A_{Me} for ketoses, +31,050, to the value of +3146 there is obtained the $[M]_D$ value for the α-methyl-*d*-glucoheptuloside pentaacetate(2,5) = +34,196. The corresponding $[\alpha]_D$ value is +34,196/434 = +78.8°. This calculated value for the derivative with the 2,5 ring is so near the observed value of +78.5° that the 2,5 ring is also assigned to the α-methyl-*d*-glucoheptuloside pentaacetate.

The specific rotation of the *d*-glucoheptulose α-hexaacetate(2,5) may be calculated in the following manner. The $[M]_D$ of *d*-glucose pentaacetate is obtained, (+55°) (390) = +21,450. From this value of +21,-450 is subtracted the value of A_{Ac} for aldoses, +19,100, giving the value of $B_{d\text{-glucose}(1,4),\ Ac}$ = +2350. Adding to the value of +2350 the value

[9] Haworth and Porter, *J. Chem. Soc.*, 2796 (1929).

of A_{Ac} from the fructose series, +30,458, there is obtained the value of +32,808, the calculated $[M]_D$ for *d*-glucoheptulose α-hexaacetate-2,5. The corresponding $[\alpha]_D$ value is +32,808/462 = +71°. This value of +71° is lower than the observed value of +87.5°, but not sufficiently different to indicate any ring but the 2,5 type in the hexaacetate. In consideration of the values of the rotations of the basal acetylated chains in derivatives of *d*-fructose and of *d*-glucoheptulose the observation has been made that the values are larger in the pentaacetates of fructose and in the hexaacetates of *d*-glucoheptulose than in the methylfructoside tetraacetates and methyl-*d*-glucoheptuloside pentaacetates by 2725 and 6896. At present no valid explanation can be given for the abnormally large value calculated for $B'_{d\text{-glucoheptulose(2,5), Ac}}$ from the hexaacetates. The question of the differences in the values of the basal acetylated chains is one peculiar to the 2-ketose sugars and can only be solved by the preparation and study of corresponding derivatives of other 2-ketoses. It is interesting to note that, using the value $B_{d\text{-glucoheptulose(2,5), Ac}}$ = +3019 (one-half the sum of the values of $[M]_D$ from the methyl-*d*-glucoheptuloside pentaacetates), one may calculate the value of the specific rotation of the α-*d*-glucose pentaacetate(1,4) by adding the value of A_{Ac} for aldoses and dividing by the molecular weight, 390, of the compound of *d*-glucose. The value calculated is $[\alpha]_D$ +56.1°, which is so near the value of +55° calculated for this substance by Hudson, from other rotations, as to warrant the suggestion that the normal value of $B_{d\text{-glucoheptulose(2,5), Ac}}$ is found by consideration of the methyl-*d*-glucoheptuloside pentaacetates rather than the hexaacetates of the ketose. The use of the value $B'_{d\text{-glucoheptulose(2,5), Ac}}$ = +9915 in a similar calculation leads to the value $[\alpha]_D$ +74.4° for the α-*d*-glucose pentaacetate(1,4). As there is no other evidence for the existence of an acetate of *d*-glucose of such rotation, the value of $B'_{d\text{-glucoheptulose(2,5), Ac}}$ must be considered abnormal, pending the preparation of similar acetates of other ketoses.

The above methods of allocation of ring structure in the derivatives of *d*-glucoheptulose may be applied to a determination of the ring in *d*-glucoheptulose itself. From one-half the sum of the $[M]_D$ values of the two forms of methyl-*d*-fructoside the value of $B_{d\text{-fructose}}$ is obtained, −12,300. If this value is subtracted from the $[M]_D$ value of β-*d*-fructose, −24,000, there is obtained the value A_{OH} for fructose, −11,700. The $[M]_D$ value of α-*d*-glucose(1,4), calculated by Hudson, is (+66°) (180) = +11,880. From this value of +11,880 the value of $B_{d\text{-glucose(1,4)}}$ = +3380 is obtained by subtraction of the value of A_{OH} for aldoses, +8500. Adding the values of +3380 and +11,700 there is obtained the calculated $[M]_D$ of α-*d*-glucoheptulose(2,5) = +15,080. The corresponding $[\alpha]_D$ value is +15,080/210 = +72°. This is so near the observed rotation, $[\alpha]_D^{20}$ +67.5°, as to constitute further proof, independent of

that in the previous paper by the writer, that the *d*-glucoheptulose which has been synthesized is of the alpha form and contains the 2,5 ring.

The specific rotation of the β-*d*-glucoheptulose may now be calculated. The value of the $[M]_D$ of α-*d*-glucoheptulose(2,5) is (+67.5°) (210) = +14,175. The value of $2A_{OH}$ from the fructose series, as derived in the preceding paragraph, is +23,400, and the difference is −9225, which is the calculated $[M]_D$ for β-*d*-glucoheptulose(2,5). The corresponding specific rotation is $[\alpha]_D = -9225/210 = -44.0°$.

Experimental Part

Preparation of α-Methyl-*d*-glucoheptuloside.—This substance was prepared by the method used by Fischer[10] in the preparation of α-methyl-*d*-glucoheptoside. *d*-Glucoheptulose, 8.4 g. of $[\alpha]_D^{20}$ +67.3°, was finely powdered and dissolved, with heating, in 100 cc. of methyl alcohol containing 1 g. of dry hydrogen chloride. The solution of the sugar was accomplished in twenty minutes of heating on the steam-bath. The reaction mixture was allowed to stand at room temperature for twelve to fourteen hours and was then freed of hydrogen chloride by warming with an excess of silver carbonate and filtering. The filtrate was diluted to 150 cc. with methyl alcohol. A quantitative copper reduction test on a 5-cc. portion of this solution showed that only 3.2% of the used ketose remained uncombined. The remaining 145 cc. of solution was concentrated to a thin sirup by evaporation under reduced pressure. After holding this sirup for several days in a desiccator over calcium chloride crystal tufts appeared. On stirring these into the sirup the entire mass became semi-crystalline. This mass was dissolved in 35 cc. of warm methyl alcohol and 500 cc. of warm acetone was added. The solution was cooled to zero, decanted from an impurity of sirup and refrigerated overnight. The next day the crop of crystals, which formed as tufts of prisms, was filtered out and dried at 37°. The precipitated sirup was worked over twice by solution in methyl alcohol and dilution with acetone, followed by cooling to zero, decantation of the cleared solution, and crystallization of more of the substance by refrigeration. The three crops of material were united to give 5.5 g., 63% of the theoretical yield. This fraction was found to have $[\alpha]_D^{20-25}$ +109.38° (0.6342 g. of substance in water to 25.0 cc. read α = +5.55°, using a 2-dm. tube). The material softened at 135° and melted at 138–140°. The remaining 4.9 g. was recrystallized from 20 cc. of warm methyl alcohol by the addition of 250 cc. of acetone, followed by refrigeration overnight. No sirup separated and the next day the mother liquor was decanted and the crystals washed with acetone by decantation and dried at 37° to 4.2 g. of substance, melting at 138–140° of $[\alpha]_D^{20-25}$ +108.78° (0.5890 g. substance in solution with water to 25.0 cc. read α = +5.13°, using a 2-dm. tube). These values did not change on further recrystallization and the $[\alpha]_D^{20-25}$ +108.5 ± 0.5°, with melting point 138–140°, are accepted as constants for the pure substance.

Anal. Estimations of OCH_3 were made on 0.3089 and 0.2160 g. samples of the substance and gave 0.3216 and 0.2295 g. of AgI, corresponding to 13.76 and 14.04% OCH_3. Calcd. for $C_8H_{16}O_7$: mol. wt., 224.12; OCH_{31} 13.84%.

The combustions[11] of 0.15 to 0.23 g. samples showed C, 42.93, 42.30; H, 7.57, 7.17; calcd.: C, 42.83; H, 7.19.

[10] Fischer, *Ber.*, **28**, 1157 (1895).

[11] All of the combustions reported herein were made by the writer in the Chemical Laboratory of the College of Liberal Arts, Northwestern University, by the kind permission of Dr. C. D. Hurd.

Preparation of α-Methyl-*d*-glucoheptuloside Pentaacetate.—A mixture of 2.3 g. of pure α-methyl-*d*-glucoheptuloside, 15 cc. of acetic anhydride, and 1.5 g. of anhydrous sodium acetate was heated for one and one-half hours on the steam-bath with frequent shaking. The solution was then poured into a mixture of ice and water, 100 g. of each. The acidity of the mixture was reduced with additions of solid sodium bicarbonate. The sirup which immediately separated hardened and crystallized in thirty minutes. The next day the crystalline material was filtered out and dried at 37° to 3.5 g. Extraction of the filtrate with chloroform resulted in the recovery of 0.2 g. more of the substance, making a yield of 87% of the theoretical. The 3.5 g. of substance was recrystallized three times from solution in 10–15 cc. of absolute alcohol by the addition of 5 volumes of water to give 2 g. of substance with a melting point of 110° and a rotation of $[\alpha]_D^{20-25}$ +78.44° (0.5466 g. substance in chloroform to 25.0 cc. read α = +3.43°, using a 2-dm. tube). A fourth recrystallization did not alter the value of the rotation or the melting point. Accordingly, the constants, $[\alpha]_D^{20-25}$ +78.5 ± 0.5°, and m. p. 110°, are accepted for the pure α-methyl-*d*-glucoheptuloside pentaacetate.

Anal. Estimations of OCH_3 were made on 0.4120 and 0.3103 g. samples of the substance, and gave 0.2337 and 0.1749 g. AgI, corresponding to 7.50 and 7.45% OCH_3. Calcd. for $C_{18}H_{26}O_{12}$: mol. wt., 434.2; OCH_3, 7.14. The combustions[11] of 0.15 g. samples of the substance showed C, 49.67, 49.58; H, 6.12, 6.30; calcd.: C, 49.75; H, 6.04. By the directions of Kunz[12] 0.3840 and 0.4081 g. samples of the substance were equivalent to 44.04 and 46.74 cc. of 0.1 *N* KOH. Calcd., 44.23, 46.99 cc.

Preparation of *d*-Glucoheptulose α-Hexaacetate.—A mixture of 10 g. of finely powdered *d*-glucoheptulose with 70 cc. of acetic anhydride and 6 g. of anhydrous sodium acetate was heated for one and one-half hours on the steam-bath with frequent shaking. The dark colored reaction mixture was then poured into a mixture of ice and water, 200 g. of each. The acidity of the mixture was reduced with additions of solid sodium bicarbonate. The dark sirup which separated slowly crystallized overnight. The soft dark mass was then filtered out and dried at 50° to 10 g. This crude product was recrystallized from solution in 15 cc. of alcohol by the addition of 7 cc. of water to give 5.5 g. of material. This material was combined with 16.0 g. of similar material made from 30 g. more of the *d*-glucoheptulose. The average yield of recrystallized acetate was approximately 25% of the theoretical, much lower than the customary yield of 60% in acetylating *d*-α-glucoheptose. Extraction of all mother liquors with chloroform and carbon tetrachloride has given no evidence of the formation of isomeric acetates. The continued darkening during the acetylation by heating the reaction mixture is indicative of decomposition of the acetate. In future preparations it is hoped that shortening the period of heating will result in a larger yield of pure product. The 21.5 g. of material was recrystallized twice from solution in three times its weight of alcohol by the addition of its weight of water, and gave 20.0 g. of hexaacetate, of $[\alpha]_D^{20-25}$ +87.8° (0.4907 g. substance in chloroform to 25.0 cc. read α = +3.45°, using a 2-dm. tube). The substance melted at 112°. A third recrystallization gave 17.5 g. of substance of $[\alpha]_D^{20-25}$ +87.08° (0.4923 g. of substance in chloroform to 25.0 cc. read α = 3.43°, using a 2-dm. tube). The melting point was unchanged, at 112°. The values $[\alpha]_D^{20-25}$ +87.0 ± 0.5°, m. p. 112°, are accepted for the pure crystalline *d*-glucoheptulose α-hexaacetate. The substance crystallizes from alcohol by the addition of water in very slender, interlaced and silky prisms. It was found that recrystallized preparations must be dried in vacuum over calcium chloride at room temperature to avoid decomposition, which is slight but detectable at 50°.

Anal. The combustions[11] of 0.15 to 0.22 g. samples of the substance showed C,

[12] Kunz and Hudson, THIS JOURNAL, **48**, 1982 (1926).

48.94, 48.99; H, 5.72, 5.77; calcd.: C, 49.32; H, 5.67. By the directions of Kunz[12] 0.5285 and 0.4592 g. samples of the substance were equivalent to 70.18 and 61.01 cc. of 0.1 *N* KOH. Calcd., 70.20 and 61.00 cc.

The author desires to thank Dr. C. S. Hudson for his helpful interest and many valuable suggestions in connection with the above contribution.

Summary

The following three new crystalline derivatives of the ketoheptose, *d*-glucoheptulose, have been prepared and purified to constant rotation and melting point: α-methyl-*d*-glucoheptuloside, $[\alpha]_D^{20-25}$ +108.5°, in water, m. p. 138–140°; α-methyl-*d*-glucoheptuloside pentaacetate, $[\alpha]_D^{20-25}$ +78.5°, in chloroform, m. p. 110°; and *d*-glucoheptulose α-hexaacetate, $[\alpha]_D^{20-25}$ +87.0°, in chloroform, m. p. 112°.

d-Glucoheptulose and *d*-fructose are alike in configuration about carbon atoms No. 1 and 2, and *d*-glucoheptulose contains about carbon atoms 3, 4, 5 and 6 the same configurations as carbon atoms 2, 3, 4 and 5 of *d*-glucose. By applying to the above-mentioned rotations and those of the corresponding derivatives of *d*-glucose the rotation coefficients of the 2-ketose series (given in large part by Schlubach and Schröter from the fructose series) and of aldoses (given by Hudson) it has been shown that the new derivatives of *d*-glucoheptulose are alpha forms and contain the 2,5 ring.

The rotations of the corresponding unknown beta forms of this sugar and its derivatives have been calculated from those of the known alpha forms by applying the rotation coefficients of the 2-ketose series.

By the use of the above rotation coefficients in connection with the rotation of *d*-glucose (1,4 ring), predicted by Hudson, the rotation of the alpha form of *d*-glucoheptulose has been calculated; the fair agreement with the observed value lends further support to the conclusion in the previous paper that the ring in the known form of this ketoheptose is 2,5. Conversely, the rotations of *d*-glucoheptulose and its derivatives, containing the 2,5 ring, lend added support to the values given by Hudson for *d*-glucose and its corresponding derivatives of the 1,4 ring.

The rotations of the alpha and beta forms of methyl-*d*-glucoheptuloside-(2,5) have also been calculated by considering the rotation coefficients of the 2-ketose series in connection with the rotations of the alpha and beta forms of ethyl-*d*-glucoside(1,4), recently prepared by Haworth and Porter. These calculated rotations agree so closely with the values found, or calculated by the other methods, that they are accepted as added confirmation that the ring in these derivatives of *d*-glucoheptulose is 2,5 and corresponds to the 1,4 ring in the new ethyl glucosides of Haworth and Porter.

CHICAGO, ILLINOIS

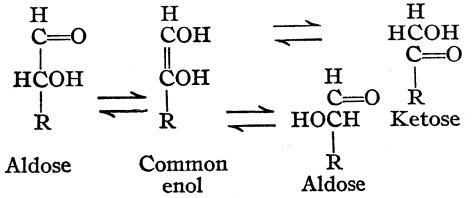
[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, LOYOLA UNIVERSITY, SCHOOL OF MEDICINE]

THE ACTION OF DILUTE ALKALI ON *d*-XYLOSE, *d*- AND *l*-ARABINOSE, *d*-α-GLUCOHEPTOSE AND *d*-GLUCOHEPTULOSE[1]

BY W. C. AUSTIN, C. J. SMALLEY AND M. I. SANKSTONE

RECEIVED NOVEMBER 9, 1931 PUBLISHED MAY 7, 1932

The recent investigations of Lewis[2] and co-workers have aroused new interest in the Lobry de Bruyn[3] conversion. Wolfrom and Lewis[2b] found that saturated calcium hydroxide induces rearrangements in sugar structures with minimal formation of caramel and saccharinic acids. Advantage was taken of this finding by Montgomery and Hudson[4] in the conversion of lactose to lactulose and by Austin[5] in the conversion of *d*-α-glucoheptose to *d*-glucoheptulose. The more widely accepted theory of the mechanism of the conversion is that the reducing sugar, when dissolved in alkali, forms a common enol which then rearranges to form new reducing sugars. The new reducing sugars so formed are predominantly those differing from the starting sugar only with respect to the configurations about the first and second carbon atoms.[6] The general structures shown in the formulas illustrate the extent and mechanism of the predominating interconversions between reducing sugars under the influence of alkali. The arrows indicate that the reactions are reversible and that the three remaining substances are formed from any one in solution with alkali.



[1] Abstracted in part from dissertations submitted by Smalley and Sankstone to the Graduate School of Loyola University in partial fulfilment of the requirements for the degree of Master of Science. A portion of the results described here was given on the program of the meeting of the American Chemical Society in Indianapolis, March 30–April 3, 1931, and on the program of the meeting of the American Society of Biological Chemists in Montreal, April 8–11, 1931. The authors desire to thank Mr. B. J. Gregory for valuable technical assistance.

[2] (a) Gustus and Lewis, THIS JOURNAL, **49**, 1512 (1927); (b) Wolfrom and Lewis, *ibid.*, **50**, 837 (1928); (c) Greene and Lewis, *ibid.*, **50**, 2813 (1928); (d) Gross and Lewis, *ibid.*, **53**, 2772 (1931).

[3] Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, **14**, 156 (1895); **14**, 195 (1895); **14**, 207 (1895); **16**, 262 (1897); **19**, 1 (1900); **27**, 1 (1908).

[4] Montgomery and Hudson, THIS JOURNAL, **52**, 2101 (1930).

[5] Austin, *ibid.*, **52**, 2106 (1930).

[6] For more complete consideration of the theories of the Lobry de Bruyn conversion, the reader is referred to the papers cited by Gross and Lewis.[2d]

With *d*-xylose as the starting sugar it would be expected from the above theory that a common enol would be formed by the action of the alkali and from it *d*-lyxose and *d*-xyloketose would next form to constitute an equilibrated system.

In like manner *l*-arabinose in solution with alkali would be expected to form a common enol which would form *l*-ribose and *l*-araboketose and constitute another equilibrated system. Also *d*-α-glucoheptose would be expected to form a common enol which in turn would give rise to *d*-β-glucoheptose and *d*-glucoheptulose and constitute a third equilibrated system.

Before beginning experiments with the purpose of isolating products of rearrangement of *d*-xylose and of *l*-arabinose, it was thought advisable to follow quantitatively the changes which these sugars undergo when dissolved in saturated calcium hydroxide. It was found that the rotation of a solution of *d*-xylose in this medium changed from $[\alpha]_D^{20-35}$ +18.2° to the constant value of $[\alpha]_D^{20-35}$ +10° in twenty-four hours at 30–35°. The P_H changed in a month of observation from 10.19 to 6.01. During this longer period the percentage of reducing pentose fell from 99.73 to 91.53% of the used *d*-xylose, while the aldose concentration decreased from 97.5 to 88.2% of the used *d*-xylose. These concentrations of reducing pentose and aldopentose indicated that at no time was more than 5% of reducing ketose evident. Solutions of *d*-xylose which have attained such equilibrium values have been freed of unchanged *d*-xylose by evaporation and crystallization, leaving sirupy residues from which as yet no *d*-lyxose or *d*-xyloketose has crystallized. One such sirup showed a rotation of $[\alpha]_D^{20-35}$ −0.26°, with 118% apparent aldose pentose, with only 70% reducing pentose. When a portion of this sirup was dissolved in saturated calcium hydroxide, it changed from $[\alpha]_D^{20-35}$ −0.26 to +2.07° in rotation in one hundred forty-four hours.

It was found that the solution of *l*-arabinose in calcium hydroxide changed in rotation from $[\alpha]_D^{20-35}$ +99.6° to the constant value of +62.2° in seventy-two hours. The P_H changed in two months from 10.8 to 5.28. During this longer period of observation the percentage of reducing pentose fell from 94.5 to 86.4% of the used *l*-arabinose, while the aldose concentration decreased from 95.02 to 82.0% of the used *l*-arabinose. These concentrations of reducing pentose and aldopentose indicated that at no time was more than 5% of reducing ketose present. Solutions of *l*-arabinose which have attained equilibrium values have been freed of unchanged *l*-arabinose by evaporation and crystallization, leaving sirupy residues from which no *l*-ribose or *l*-araboketose has crystallized. A sirup so prepared has shown $[\alpha]_D^{20}$ +4.73° with 78.36% reducing pentose and 75.7% aldose pentose. Attempts to form the known *p*-bromophenylhydrazone of *l*-ribose from such sirups have met with uniform failure. Portions of the

sirups have been oxidized with bromine and the reaction products used in futile attempts to form the known phenylhydrazide and the cadmium salt of *l*-ribonic acid.

By solution of *d*-arabinose in saturated calcium hydroxide, the initial value of $[\alpha]_D^{20-35}$ −100.4° changed in ninety-six hours to $[\alpha]_D^{20-35}$ −54.4°. Evaporation of this solution and removal of unchanged *d*-arabinose by crystallization left a sirup with the value of $[\alpha]_D^{20-35}$ −7.4°. This sirup showed 74.04% of reducing pentose and 60.32% of aldopentose. A portion of this sirup was dissolved in saturated calcium hydroxide and the rotation changed very slightly in one hundred twenty hours to the constant value of $[\alpha]_D^{20-35}$ −4.9°. Another portion of this sirup was seeded with *d*-ribose without any crystallization of this pentose resulting.

In contrast with the apparent lack of reversibility between *d*-xylose and its products, and between *d*-arabinose and its products, it has been found that alkali forms *d*-α-glucoheptose from *d*-glucoheptulose in a reversible manner. With either of these heptoses as the starting material in solution with alkali the final equilibrium value of $[\alpha]_D^{20-35}$ +40 to +45° is attained. In the equilibrium mixture from the *d*-glucoheptulose there is about 23% aldose and 77% ketose. Resaturation of such an equilibrated solution with calcium hydroxide caused the value of the $[\alpha]_D^{20-35}$ +45° to decrease further to the constant value of $[\alpha]_D^{20-35}$ +36°, when the solution contained 42% aldose and 58% ketose.

Experimental Part

The Action of Dilute Alkali on *d*-Xylose.—*d*-Xylose (37.5 g. with $[\alpha]_D^{20}$ +19.9°) was dissolved in calcium hydroxide solution, previously saturated at 30–35° and filtered, to make 500 cc. of solution, half-molal in concentration of the sugar. Before the sugar was dissolved the P_H of the solution of calcium hydroxide was 12.3, determined potentiometrically with the hydrogen electrode. Five minutes after solution of the *d*-xylose in this medium the P_H was 10.19. A portion of the solution was used to fill a 2-dm. tube and found to have the value of $[\alpha]_D^{20-35}$ +18.19°, five minutes after the solution of the sugar. A second portion of the solution was diluted and used for the iodine titration by the directions of Goebel,[7] employing a fifteen-minute oxidation time. This estimation accounted for 97.56% of the used *d*-xylose, five minutes after solution. At the same time interval a portion of the diluted solution was used to estimate the total reducing pentose by the directions of Bertrand,[8] and showed the value of 99.73% of the used *d*-xylose. The solution was preserved with xylene and kept at 30–35°. From time to time other portions of this stock solution were withdrawn for repetition of the analyses, with the addition of iodine oxidations on portions of the solution which had been deenolized by the directions of Wolfrom and Lewis,[2b] holding the sample in 2 *N* sulfuric acid for twenty-four hours before neutralization and oxidation with iodine in the usual manner. The changes in the solution are shown in Table I, and graphically in Fig. 1.

Further Studies of the Products from *d*-Xylose.—A solution, containing in 1180 cc. the products of the action of calcium hydroxide on 88.5 g. of *d*-xylose, was clarified and

[7] Goebel, *J. Biol. Chem.*, **72,** 801 (1927).

[8] Bertrand, *Bull. soc. chim.*, **35,** 1285 (1906).

TABLE I

CHANGES OF *d*-XYLOSE IN DILUTE ALKALI AT 30–35°

Time, hours	$[\alpha]_D^{20-35}$ [a]	Aldopentose, % A [b]	Aldopentose, % B [c]	Reducing pentose, %	P_H
0.08	18.19	97.56		99.73	10.19
.66	18.33				10.06
2.5	16.20				9.93
2.8		100.60	100.83	97.53	
4.5	13.72				9.01
5.6		100.60	96.92	97.33	
24.0	10.20	93.60	91.52	93.80	
51.0	10.41				9.24
72.0	10.35	90.40	90.29	93.33	9.65
142.0	10.01		88.39	92.23	7.69
166.0		87.30		92.0	
720.0	10.40	88.26	91.24	91.53	6.01

[a] $C = M/2$ solution of *d*-xylose in 0.04 *N* calcium hydroxide. [b] Before de-enolization. [c] After de-enolization.

evaporated to a thick sirup under reduced pressure. The sirup was diluted with 20 cc. of water and 480 cc. of hot methyl alcohol, filtered from an amorphous precipitate, and again reduced by evaporation to a sirup under reduced pressure. This sirup was thinned with 90–95% ethyl alcohol and allowed to crystallize overnight. Eighteen g. of

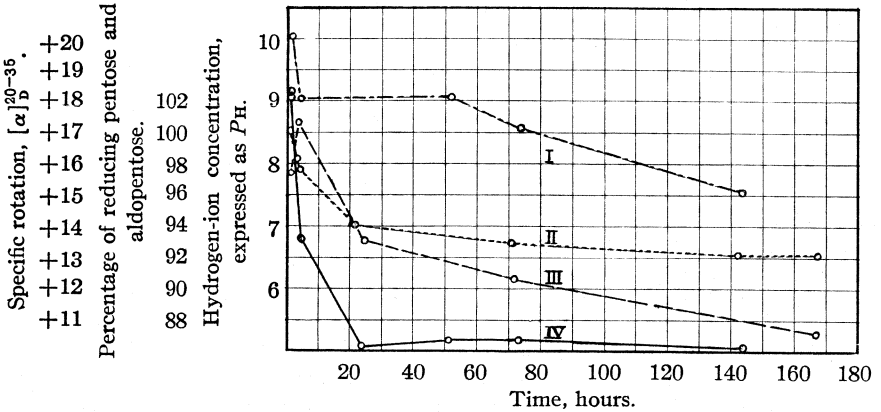


Fig. 1.—Changes in a solution of 37.5 g. of *d*-xylose in 0.04 *N* calcium hydroxide to 500 cc., at 30–35°: I, change in P_H; II, change in percentage of reducing pentose; III, change in percentage of aldopentose; IV, change in specific rotation, $[\alpha]_D^{20-35}$.

crude *d*-xylose was then removed by filtration. Concentration of the filtrate gave 6.0 g. more of crystalline *d*-xylose in three crops. The mother liquor of the last crop was dissolved in 50 cc. of methyl alcohol and the solution then diluted with 200 cc. of anhydrous ether. After one hour the supernatant solution was decanted from the hygroscopic brown precipitate and evaporated to a very clear and lightly colored sirup, from which 1.0 g. more of *d*-xylose was crystallized and removed. The sirup was then dried in a vacuum desiccator to 11.2 g. A sample of 1.9316 g. of the purified sirup was dissolved in water to 50 cc. A portion of this solution was saturated with calcium hydroxide and filtered into a 2-dm. tube for the reading $\alpha = -0.03°$, corresponding to $[\alpha]_D^{20-35}$

$-0.26°$. Seventy-two hours later the value was $[\alpha]_D^{20-35}$ $+1.67°$, and in 144 hours $+2.07°$. Before the solution was saturated with calcium hydroxide, the apparent aldopentose was 118.1%, with 69.37% reducing pentose. At the end of the one hundred and forty-four hour period the apparent aldopentose was 46.79%, with 45.72% reducing pentose.

The Action of Dilute Alkali on *l*-Arabinose.—*l*-Arabinose (37.5 g., $[\alpha]_D^{20}$ $+101.5°$) was dissolved in calcium hydroxide solution, previously saturated at 30–35° and filtered, to make 500 cc. of solution, half-molal in concentration of *l*-arabinose. Before the sugar was dissolved the P_H of the calcium hydroxide was 12.3, determined potentiometrically by the hydrogen electrode method. Twenty-five minutes after solution of the sugar the P_H was 10.80. A portion of the solution was used to fill a 2-dm. tube and found to have the value of $[\alpha]_D^{20-35}$ $+99.6°$. At the same time interval a second portion of the solution was used for the iodine titration by the method of Goebel,[7] employing fifteen minutes' time for oxidation. This estimation accounted for 95.02% of the used *l*-arabinose as aldopentose. A portion of the diluted solution was held for twenty-four hours in 2 *N* sulfuric acid, the solution then neutralized and oxidized with iodine in the usual manner. This estimation on the de-enolized sample accounted for 96.43% of the used *l*-arabinose as aldopentose. At the same time interval, twenty-five minutes after solution of the sugar, another portion of the diluted solution showed 94.56% of the used *l*-arabinose as reducing pentose, using the directions of Bertrand.[8] The remaining solution was preserved with xylene and kept at 30–35°. From time to time portions of this stock solution were withdrawn for repetition of the mentioned examinations. The changes in the *l*-arabinose are shown in Table II, and graphically in Fig. 2.

TABLE II

CHANGES OF *l*-ARABINOSE IN DILUTE ALKALI AT 30–35°

Time, hours	$[\alpha]_D^{20-35}$ [a]	Aldopentose, % A [b]	Aldopentose, % B [c]	Reducing pentose, %	P_H
0.42	99.60	95.02	96.43	94.56	10.80
3.25	95.23				
5.08		96.08	96.28	93.60	10.63
6.60	88.27				
9.00	85.20				
23.30	70.66	88.27	87.97	88.27	10.10
29.66	69.14				
47.00		85.33	83.84	87.20	9.60
48.33	65.00				
71.10	62.20				
119.20		82.40	83.69	86.27	7.84
191.20	61.66	81.24	82.51	85.43	7.21
1614.25	61.87	82.00	78.20	86.40	5.28

[a] $C = M/2$ solution of *l*-arabinose in 0.04 *N* calcium hydroxide. [b] Before de-enolization. [c] After de-enolization.

Further Studies of the Products from *l*-Arabinose.—Sixty grams of *l*-arabinose of $[\alpha]_D^{20}$ $+101.8°$ was dissolved in saturated calcium hydroxide solution and allowed to change to the final constant value $[\alpha]_D^{20-35}$ $+56.7°$ in seven days. The solution was then evaporated to a sirup under reduced pressure, diluted with 400 cc. of methyl alcohol, and filtered from an amorphous precipitate of 7 g. The filtrate was concentrated to a sirup again and allowed to crystallize overnight. Twenty grams of crude sugar was filtered out and recrystallized to 15.6 g. of crude *l*-arabinose of $[\alpha]_D^{20}$ $+97.7°$. From the sirup

5.2 g. more of *l*-arabinose was crystallized in three crops. The sirup was no longer crystallizable and showed the rotation of $[\alpha]_D^{20}$ +5.34° (0.6544 g. in water to 25 cc. to read α = +0.28°, using a 2-dm. tube). The sirup was diluted with 300 cc. of methyl alcohol and 300 cc. of anhydrous ether and the solution then filtered with carbon from an amorphous colored precipitate of 3 to 5 g. The solution was again reduced to a sirup from which 0.6 g. more of *l*-arabinose was removed after crystallization. The residual sirup showed $[\alpha]_D^{20}$ +4.73° (0.8455 g. in water to 25 cc. for reading α = +0.32°, using a 2-dm. tube). The sirup showed 78.36% of reducing pentose and 75.7% of aldopentose. The remaining 7.5 g. of the sirup was mixed with 5 g. of *p*-bromophenylhydrazine and 35 cc. of absolute alcohol. The mixture did not form any *l*-ribose *p*-bromophenylhydrazone crystals in forty-eight hours at 30–35°, as described by Fischer and Piloty.[9] The solution was freed of alcohol by evaporation and diluted with 300 cc. of water containing 19 cc. of 50% acetic acid, 20 g. more of *p*-bromophenylhydrazine hydrochloride and 15.0 g. of sodium acetate. No *l*-ribose *p*-bromophenylhydrazone formed in one hour of

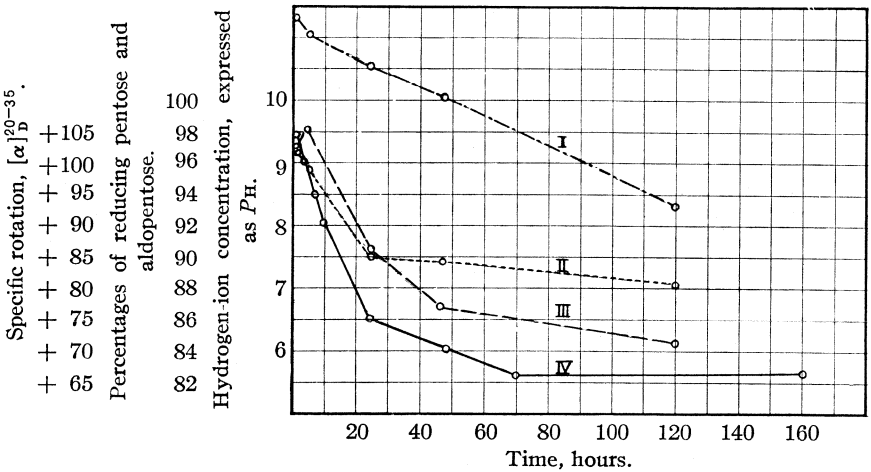


Fig. 2.—Changes in a solution of 37.5 g. of *l*-arabinose in 0.04 *N* calcium hydroxide to 500 cc. at 30–35°: I, change in P_H; II, change in percentage of reducing pentose; III, change in aldopentose; IV, change in specific rotation, $[\alpha]_D^{20-35}$.

standing as described by van Ekenstein and Blanksma[10] so 20 g. of *l*-arabinose in 30 cc. of water was added. The *l*-arabinose *p*-bromophenylhydrazone began to crystallize in two minutes. After one and one-half hours this insoluble hydrazone was filtered off and dried to 30 g., the customary yield from *l*-arabinose.

By the action of calcium hydroxide solution on 80 g. of *l*-arabinose, followed by removal of 26 g. of unchanged *l*-arabinose by crystallization, and purification of residual sirup, there was prepared 16 g. of sirup of $[\alpha]_D^{20}$ +10.1°. This sirup was oxidized by the directions of Hudson and Isbell[11] to form sugar acids of any remaining aldose and the solution freed from benzoate, bromide and silver ions. The solution of about 80 cc. was divided into two equal parts, each containing 3 to 4 g. of aldonic acids by estimate.

[9] Fischer and Piloty, *Ber.*, **24**, 4214 (1891).

[10] Van Ekenstein and Blanksma, *Chem. Centr.*, II, 1562 (1915); *Chem. Weekblad*, **10**, 664 (1913).

[11] Hudson and Isbell, THIS JOURNAL, **51**, 2225 (1929).

One portion was heated with an excess of cadmium hydroxide suspension, according to the directions of Fischer and Piloty,[9] who have described the crystalline cadmium salt of *l*-ribonic acid. The solution was filtered from the excess of base and evaporated to a brown sirup which contained dissolved cadmium, but which has deposited no crystalline salt of *l*-ribonic acid. The second portion of the solution suspected of containing *l*-ribonic acid was evaporated on the steam-bath, after the addition of 5 g. of phenylhydrazine, to a sirup which was heated for one hour longer in an attempt to form the *l*-ribonic acid phenylhydrazide described by Fischer and Piloty.[9] The mass deposited only a brown tarry residue on dilution with water. Attempts to crystallize material from this mass with the use of various solvents have resulted in uniform failure.

The Action of Dilute Alkali on *d*-Arabinose.—By the process of Clark[12] and Ruff,[13] degradation of calcium gluconate with 3% hydrogen peroxide and ferric acetate, 267 g. of pure *d*-arabinose was made with a yield of 11%. The *d*-arabinose showed $[\alpha]_D^{20}$ −103.7°, with m. p. 154–156°. The 267 g. of the sugar was dissolved in saturated calcium hydroxide to the volume of 3780 cc. Readings on a portion of the solution, kept at 30–35°, were $[\alpha]_D^{20-35}$ −100.4° after fifteen minutes, −68.2° after twenty-two hours, −55.1° after seventy hours, and constant at −54.4° after ninety-four hours. The solution was then clarified with carbon and concentrated to 170 cc. of sirup under reduced pressure. This sirup was diluted with 220 cc. of methyl alcohol and, after three days of refrigeration, filtered from 133 g. of *d*-arabinose of $[\alpha]_D^{20}$ −99.5°, m. p. 148–149°. The mother liquor and washes were concentrated to 75 cc., diluted with 250 cc. of methyl alcohol and saturated with 60 cc. of absolute alcohol. Two grams more of *d*-arabinose was crystallized and removed. The filtrate was seeded with *d*-ribose[14] without any crystallization being induced. The solution was held in the refrigerator for several days and did not crystallize. It was then diluted to 500 cc. with methyl alcohol and a 25-cc. portion evaporated under reduced pressure in a tared beaker to a residue of 5.1804 g., indicating that 100 to 105 g. of sirup was produced from the 267 g. of *d*-arabinose by rearrangement. The 5.1804 g. of sirup was dissolved in water to 50 cc. for reading ($[\alpha]_D^{20}$ −6.99°, α = −1.45°, using a 2-dm. tube). Analyses of this solution showed that the sirup contained 74.04% of reducing pentose and 60.32% of aldopentose. A solution of 1.2951 g. of this sample of sirup in 25 cc. of water was saturated with calcium hydroxide and showed $[\alpha]_D^{20-35}$ −7.42° fifteen minutes after saturation, −6.17° twenty-four hours later, and −4.91°, constant, one hundred and forty-four hours after saturation. The reducing pentose had decreased to 67.72% of the sample and the aldopentose to 56.49%.

The remaining larger portion of the solution of 95 to 100 g. of the sirup was evaporated under reduced pressure to a thick sirup of 90 cc. This was thinned with 35 cc. of methyl alcohol and 10 cc. of absolute alcohol and again seeded with *d*-ribose. Beyond the formation of 6 g. more of crystalline *d*-arabinose, no crystallization has occurred in three months.

The Action of Dilute Alkali on *d*-α-Glucoheptose and α-Glucoheptulose.—In order to determine whether the reaction *d*-α-glucoheptose ⟷ *d*-glucoheptulose is reversible in dilute alkali, a 10% solution of *d*-glucoheptulose in saturated calcium hydroxide was made at 30–35°. The $[\alpha]_D^{20-35}$ changed from an initial rotation of $[\alpha]_D^{20}$ +67.4°, the value of the ketose, to +66.9° in three hours, +64.7° in five hours, +55.9° in twenty-two hours, and became constant in one hundred and twenty hours at +45.4°. An iodine estimation of aldoses in this solution showed 23% aldoses, with 77% ketoses. The remainder of the solution was resaturated with alkali and the $[\alpha]_D^{20-35}$ value decreased

[12] Clark, *J. Biol. Chem.*, **31**, 605 (1921).

[13] Ruff, *Ber.*, **32**, 554 (1899).

[14] We are indebted to Mr. F. P. Phelps, U. S. Bureau of Standards, who kindly supplied crystalline *d*-ribose for this use.

further over six days to a new equilibrium rotation of +35.0°. The solution now showed that 42% of the ketose had been transformed to aldose capable of iodine consumption. The balance of 58% of unchanged ketose was shown by difference. These results are compared graphically in Fig. 3 with those published by Austin[5] on the extent of change of *d*-α-glucoheptose in dilute alkali. Taken together the results indicate reversibility of the interconversion between *d*-α-glucoheptose and *d*-glucoheptulose.

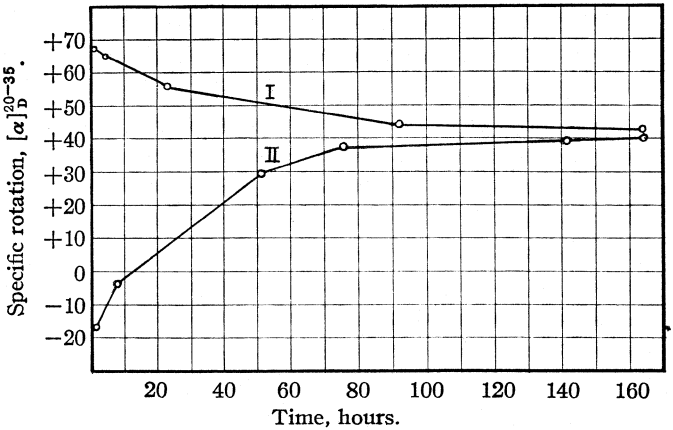


Fig. 3.—Changes in specific rotations of half-molar solutions of *d*-glucoheptulose and *d*-α-glucoheptose in 0.04 *N* calcium hydroxide, at 30–35°: I, *d*-glucoheptulose; II, *d*-α-glucoheptose.

In Table III is shown a summary of the changes observed in these sugars and their products by solution in saturated calcium hydroxide.

TABLE III

SUMMARY OF CHANGES CAUSED BY DILUTE ALKALI AT 30–35°

Substance	$[\alpha]_D^{20-35}$ Initial	$[\alpha]_D^{20-35}$ Final	Percentages of Reducing sugar Initial	Reducing sugar Final	Aldose Initial	Aldose Final
d-Xylose	+ 18.2	+10.0	99.7	91.5	98.5	88.2
Sirup from *d*-xylose	− 0.26	+ 2.1	70.0	46.0	118.0	47.0
l-Arabinose	+ 99.6	+60.0	95.0	86.4	95.0	82.0
Sirup from *l*-arabinose	+ 4.73		79.0		75.0	
d-Arabinose	−100.4	−54.4				
Sirup from *d*-arabinose	− 7.4	− 4.9	74.0	68.0	60.0	56.0
d-α-Glucoheptose	− 20.0	+40.0			99.0	40.0
d-Glucoheptulose	+ 67.5	+45.0 (35)[a]			0.0	23.0 (42.0)[a]

[a] The values shown in parentheses represent further changes observed after resaturation of the equilibrated solution with calcium hydroxide.

Discussion

Assuming that *d*-xylose formed only *d*-lyxose in alkali, it was calculated that the equilibrium mixture contained about 24% of the used *d*-xylose as *d*-lyxose, from a consideration of the rotation of the system and those of the two sugars. By similar assumptions the equilibrium mixture from

l-arabinose was calculated to contain about 37% of the used *l*-arabinose as *l*-ribose. These calculations are proved to be unwarranted by the behavior of the sirups from the two pentoses and by the findings of Gross and Lewis[2d] that polymerized xyloketose is present in the equilibrium mixture from *d*-xylose. A polymerized ketose of the nature described by Gross and Lewis would not be fully detected by the Bertrand copper reduction procedure, calculating results in terms of percentage of used *d*-xylose. The iodine titrations and copper reduction values are subject to the criticism that it is possible that still other substances than aldopentoses and reducing pentoses may have been present in small quantity to react with the reagents and introduce error. Thus Gross and Lewis have isolated the xyloketose in yield of 9.8% of the used *d*-xylose, while our results indicate that only about 5% of the used *d*-xylose was transformed into reducing ketose. Gross and Lewis have confirmed the findings of van Ekenstein and Blanksma[15] that *d*-lyxose is also formed from *d*-xylose by the action of dilute alkali, although the *d*-lyxose was not crystallized as such by either group of investigators. Although Gross and Lewis have employed molar solutions of *d*-xylose for rearrangement as compared with half molar in our experiments, the final rotations and quantitative studies on each system indicate formation of mixtures of the same nature.

The apparently slight degree of reversibility between the pentoses and the sirups produced from them by the action of alkali, and the apparently large degree of reversibility between the *d*-α-glucoheptose and *d*-glucoheptulose, are indications that the composition of the equilibrium mixture is determined to a large extent by the nature of the sugar dissolved in the alkali. Spoehr and Strain[16] have observed that *d*-glucose, *d*-mannose, and *d*-fructose are mutually interconvertible by the action of a weakly alkaline disodium phosphate solution. They have found, however, that the compositions of the equilibrium mixtures are determined by the nature of the sugar dissolved in the weak alkali.

Before it can be concluded that the systems *l*-arabinose $\longleftrightarrow$ *l*-ribose and *d*-xylose $\longleftrightarrow$ *d*-lyxose are not reversible by the action of the solution of calcium hydroxide, further experiments with *l*-ribose and *d*-lyxose as starting sugars are desirable. It is quite possible that these crystalline sugars would exhibit greater reversibility than the sirups made from *d*-arabinose and *d*-xylose have shown.

We have been unable to confirm the findings of van Ekenstein and Blanksma[17] that *l*-arabinose is partially transformed into *l*-ribose in alkaline solution. These workers have heated the *l*-arabinose in normal sodium hydroxide and then oxidized the mixture to *l*-arabonic and *l*-ribonic acids.

[15] Van Ekenstein and Blanksma, *Chem. Weekblad*, **11**, 182 (1914).

[16] Spoehr and Strain, *J. Biol. Chem.*, **85**, 370 (1929).

[17] Van Ekenstein and Blanksma, *Chem. Weekblad*, **10**, 213–214 (1913).

The *l*-ribonic acid was separated from the *l*-arabonic acid by fractional crystallization of the mixed phenylhydrazides. We have employed 0.04 *N* calcium hydroxide, removed unchanged *l*-arabinose, oxidized the remaining sirup and attempted to form by their directions the phenylhydrazide of *l*-ribonic acid without success. In the light of our further negative experiments of seeding with *d*-ribose the sirups from the rearrangement of *d*-arabinose, the different findings can at present be best explained as due to differences in the temperatures, nature of the alkali and concentrations.

The authors are pleased to note here the recent findings of Neher and Lewis[18] on changes of a solution of *l*-arabinose in calcium hydroxide. Although they have studied changes in a molar solution of this sugar with respect to rotation and content of aldopentose, while we have measured changes of a half-molar solution with regard to rotation, contents of aldopentose and reducing pentose, and P_H, the results given by the two independent studies are close agreement.

The authors desire to thank Dr. C. S. Hudson for his helpful interest and valuable suggestions in connection with the above studies.

Summary

1. When a half molal solution of *d*-xylose was made in saturated calcium hydroxide at 30–35° the value of the $[\alpha]_D^{20-35}$ changed in twenty-four hours from +18.2° to the constant value of +10.2°. The P_H of the solution decreased more slowly from 10.19 to 6.01 during one month. The percentages of the reducing pentoses and of the aldopentoses decreased slowly from initial values of 99.73 and 97.5 to 91.53 and 88.20 during the month. The sirup prepared from *d*-xylose by the action of the alkali was dissolved again in calcium hydroxide solution and changed slightly from $[\alpha]_D^{20}$ −0.26° to +2.0° in one hundred forty-four hours, indicating very little reversibility toward the equilibrium value obtained from *d*-xylose.

2. When a half-molal solution of *l*-arabinose was made in saturated calcium hydroxide at 30–35°, the value of $[\alpha]_D^{20-35}$ changed in seventy-two hours from +100.0° to the constant value of +62.0°. The P_H of the solution decreased more slowly from the initial value of 10.8 to 5.28 during seventy days. The percentages of the reducing pentoses and of the aldopentoses decreased from beginning values of 94.5 and 95.0 to 86.4 and 82.0 during the seventy days. Sirups prepared from *d*- and *l*-arabinose by the action of the alkali have not been convertible to crystalline ribose, ribose *p*-bromophenylhydrazone, or to crystalline derivatives of ribonic acid (phenylhydrazide or cadmium salt). A sirup prepared from *d*-arabinose by the action of the alkali was dissolved again in calcium hydroxide solution. The $[\alpha]_D^{20-35}$ changed slightly from the initial value of

[18] Neher and Lewis, THIS JOURNAL, **53**, 4411 (1931).

$-7.5°$ to $-5.0°$ during five days, indicating very little reversibility toward the equilibrium value obtained from *d*-arabinose.

3. In contrast to the very small reversibility in the pentose systems, *d*-α-glucoheptose and *d*-glucoheptulose are mutually interconvertible by the action of saturated calcium hydroxide solution to give a common equilibrium value of $[\alpha]_D^{20-35}$ of approximately 45.0°.

CHICAGO, ILLINOIS

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

CERTAIN FACTORS INFLUENCING THE YIELD OF GRIGNARD REAGENTS AND THE RATIO OF R_2Mg TO RMgX

BY GEORGE O. JOHNSON AND HOMER ADKINS

RECEIVED NOVEMBER 16, 1931 PUBLISHED MAY 7, 1932

The ratio of Grignard reagent to hydrocarbon formed in the reaction of magnesium with alkyl halides is in part determined by the presence of compounds other than the two essential components of the reaction mixture. Metallic chlorides have long been known to modify this ratio of Grignard to Wurtz reactions and more recently copper has been shown to exert a similar influence.[1,2] It has sometimes been assumed that the hydrocarbon formation was dependent upon the reaction of the Grignard reagent with some of the alkyl halide which had not yet reacted with magnesium as illustrated in equation 1.

$$RMgX + RX \longrightarrow R_2 + MgX_2 \qquad (1)$$

Equation 1 represents a reaction known to occur, for example, between allylmagnesium bromide and allyl bromide.[3]

It has become increasingly evident that the Grignard reagent in many cases is not exclusively or even predominantly in the form RMgX but rather as R_2Mg, these compounds being in more or less stable combination with MgX_2 and the solvent.[4,5,6,7] Therefore, a possible explanation of the effect of copper in modifying the ratio of the Grignard and Wurtz reactions is that it modifies the ratio of RMgX and R_2Mg, thus increasing the amount of the former available for the reaction represented in equation 1. This explanation of the effect of copper upon the proportion of products would rest on the further assumption that R_2Mg does not react as rapidly, if at all, with RX. The foregoing hypothesis has now been tested.

[1] Johnson and Adkins, THIS JOURNAL, **53**, 1520 (1931).
[2] Gilman and Zoellner, *ibid.*, **53**, 1581 (1931).
[3] Späth, *Monatsh.*, **34**, 1965 (1913).
[4] Schlenk and Schlenk, *Ber.*, **62B**, 920 (1929).
[5] Gilman and Fothergill, THIS JOURNAL, **51**, 3149 (1929).
[6] Noller, *ibid.*, **53**, 635 (1931).
[7] Schlenk, *Ber.*, **64B**, 734 (1931).

The yields of active Grignard reagent and of R_2Mg for sixteen alkyl halides with pure magnesium and with magnesium–copper alloy have been determined. It has been ascertained previously that the only reactions of any consequence occurring under the experimental conditions used in this work are the Grignard reagent formation and the Wurtz reaction, so that the extent of the latter is given by the difference between 100% and the figures given for the yield of Grignard reagent, except in the case of the more inactive chlorides. The determination of the effect of various experimental conditions upon the ratio of the Grignard and Wurtz reactions was made as previously described.[1] The amount of R_2Mg in the Grignard reagent was determined in general according to the method of Schlenk as modified by Noller. A summary of the experimental data is presented in Table I. The alkyl halides have been arranged in the order of the magnitude of the effect of copper in modifying the yield of Grignard reagent.

TABLE I

THE EFFECT OF COPPER UPON THE FORMATION OF THE GRIGNARD REAGENT

Alkyl halide	Yield of Grignard reagent, % Mg (pure)	Mg–Cu	Grignard reagent as R_2Mg, % Mg (pure)	Mg–Cu	Effect of Cu Upon total	Upon R_2Mg
Allyl bromide	72.3 ±0.2 (2)	5.7 ±2.0 (6)	49.4 ±3.6 (2)	.....	−67	...
Benzyl bromide	83.8 ±0.2 (2)	49.4 ±1.9 (3)	70.5 ±2.5 (3)	49.2 ±6.6 (4)	−34	−21
Ethyl bromide	93.1 ±0.8 (2)	62.4 ±1.0 (2)	42.2 ±1.8 (3)	30.2 ±0.4 (2)	−31	−12
β-Phenylethyl bromide	91.6 ±0.1 (2)	73.4 ±1.0 (2)	76.0 ±2.2 (4)	75.4 ±2.8 (4)	−18	0
Cyclohexyl bromide	79.8 ±0.4 (2)	64.4 ±3.2 (2)	81.6 ±1.7 (2)	72.9 ±1.2 (2)	−15	− 8
Isobutyl bromide	87.5 ±0.9 (5)	73.6 ±2.1 (2)	79.7 ±1.8 (6)	76.0 ±3.3 (2)	−14	− 4
n-Butyl bromide	91.8 ±0.4 (2)	74.9 (1)	81.6 ±1.7 (2)	76.9 (1)	−17	− 5
Benzyl chloride	93.6 ±0.7 (2)	76.5 ±4.0 (3)	73.4 ±2.5 (2)	72.8 ±6.1 (3)	−17	0
Ethyl iodide	86.6 ±2.3 (3)	72.5 ±1.7 (2)	6.9 ±2.7 (3)	5.9 ±1.9 (2)	−14	− 1
n-Butyl chloride	91.3 ±1.0 (2)	79.5 ±0.5 (2)	84.2 ±1.5 (2)	81.6 ±1.6 (3)	−12	− 2
n-Butyl iodide	82.1 ±0 (2)	74.3 ±1.1 (2)	76.7 ±1.4 (3)	62.6 ±7.9 (2)	− 8	−14
n-Heptyl bromide	80.6 ±1.0 (2)	72.8 ±1.3 (2)	66.8 ±9.1 (2)	72.8 ±6.8 (2)	− 8	+ 6
Phenyl bromide	94.7 ±0.5 (3)	92.3 ±1.5 (2)	75.8 ±2.7 (3)	81.5 ±3.2 (2)	− 2	+ 6
Tert.-butyl bromide	23.7 ±1.5 (2)	27.1 ±1.1 (2)	39.4 ±2.6 (2)	39.3 ±2.8 (3)	+ 3	0
Tert.-butyl chloride	28.1 ±0.5 (2)	43.4 ±1.7 (2)	62.2 ±2.8 (3)	74.9 ±0.5 (2)	+15	+13
Tert.-amyl chloride	25.3 ±0.3 (2)	38.6 ±0 (2)	67.7 ±1.2 (3)	71.1 ±1.1 (2)	+13	+ 3

The effect of copper upon the course of the reaction of magnesium with the halides may be summarized as follows. The presence of copper in the magnesium decreased the yield of the Grignard reagent in the case of all of the primary and secondary halides, the depression of the yield varying from 66.6% in the case of allyl bromide to 2.4% in the case of phenyl bromide. The depressing effect of the copper was more marked with the bromides than for the chlorides, and more for the chlorides than for the iodides. Copper very definitely raised the yield of Grignard reagent from the three tertiary halides, the effect being more in the case of tertiary butyl chloride than it was in the case of the bromide. The potency of copper in depressing the Grignard reaction decreased with increasing length of chain in the alkyl halide.

The proportion of active Grignard reagent existing as R_2Mg was in nine cases very definitely modified when copper was added to the magnesium. The magnitude of the effect of copper upon the proportion of R_2Mg (column 7 of table) was in general less than it was upon the yield of Grignard reagent (column 6 of table). However, the sign of the effect, except for heptyl and phenyl bromide, was the same for both phenomena, *i. e.*, when copper brought about a considerable decrease in the yield of Grignard reagent it also brought about a decrease in the proportion of R_2Mg, and when copper increased the Grignard reaction it also increased the proportion of R_2Mg.[8]

The question now arises as to the rate at which alkyl halides react with the Grignard reagents prepared from them, and also with the corresponding solution of R_2Mg. In order to test this point Grignard reagents were prepared from twelve halides. Four aliquots were removed from each reaction mixture. The first two were analyzed for total Grignard reagent and R_2Mg, respectively. The third aliquot was treated with a small excess of the corresponding alkyl halide. An excess of alkyl halide was also added to the solution of R_2Mg from the fourth aliquot, from which the RMgX had been precipitated with dioxane. The two solutions containing the allyl halide were then refluxed for ten minutes and the residual active Grignard reagent in each determined in the usual manner, *i. e.*, by hydrolyzing and titrating the basicity so developed.

TABLE II

THE EFFECT OF ADDED RX ON SOLUTIONS OF GRIGNARD REAGENTS AND OF DIALKYL MAGNESIUM

Halide	Change in amount Of Grignard reagent	Of R_2Mg
Allyl bromide	−50.0±3.5 (2)	−7.8 (1)
Allyl bromide[a]	−31.9±3.1 (3)	−8.0±1.4 (3)
Ethyl bromide	− 0.7±0.7 (2)	−3.9 (1)
Ethyl iodide	+ 2.0±3.0 (3)	+3.5±3.0 (3)
n-Butyl bromide	− 0.2 (1)	+1.5 (1)
Isobutyl bromide	+ 1.3±1.0 (6)	+1.7±1.6 (4)
n-Butyl chloride	0	−4.3 (1)
n-Butyl iodide	+1.8±2.0 (4)	+5.0±5.0 (4)
n-Heptyl bromide	−1.0 (1)	...
Cyclohexyl bromide	−2.5±2.0 (5)	−2.8±2.2 (3)
Phenyl bromide	−0.4±0.1 (2)	−3.5±3.1 (2)
Benzyl bromide	− 0.4±0.6 (2)	...
Benzyl chloride	− 5.5±2.0 (6)	−3.5±6.5 (5)

[a] Zinc dust was added to the reaction mixture.

The data so obtained are summarized in Table II. These data show: (1) that allyl bromide reacted to a considerable extent with the Grignard

[8] Data are not available to show what effect, if any, the concentration of the Grignard reagent in the ether has upon the ratio of R_2Mg to RMgX.

reagent prepared from it under the conditions under which the latter is formed; (2) that diallyl magnesium reacted very slowly, if at all, with allyl bromide; (3) that in the case of the other halides there was little if any reaction of either the Grignard reagent or R_2Mg with the corresponding alkyl halide. It is true that for certain pairs of reactants there was a decrease in the amount of R_2Mg or Grignard reagent. However, the magnitude of the changes and the variations in duplicate analyses rob these changes of any significance.

There are recorded in Table III data which indicate the effect of zinc and mercuric chloride upon the yield of Grignard reagent and the proportion of it which is in the form R_2Mg. These data show that the addition of zinc to the reaction mixture increased the yield of the Grignard reagent in the case of allyl bromide, but was without effect upon the other halides. Mer-

TABLE III

EFFECT OF VARIOUS METALLIC CHLORIDES AND ZINC UPON THE FORMATION OF THE GRIGNARD REAGENT[a]

Alkyl halide	Yield of reagent, %	Reagent as R_2Mg, %	Change in yield of reagent,[b] %	Change in R_2Mg,[b] %
Allyl bromide[d]	80+2.1 (8)	46+1.2 (3)	+ 8	− 3
Ethyl iodide[d]	90	...	− 1	..
Isobutyl bromide[e]	88+0.6 (2)	76+1.0 (2)	+ 1	− 4
n-Butyl iodide[e]	83	61	+ 1	−15
Cyclohexyl bromide[f]	82+0.1 (2)	68	− 1	..
Cyclohexyl bromide[g]	41	53	−37	−28
Cyclohexyl bromide[h]	44	...	−20	..
Tert.-butyl bromide[g]	15	20	− 9	−19
Benzyl bromide[g]	90	70	+ 6	0
Benzyl bromide[h]	64	63	+14	+13
Benzyl chloride[g]	94	70[c]	+ 1	+ 5
Benzyl chloride[h]	91+0.5 (4)	81	+12	+ 9

[a] The following changes in the yield of Grignard reagents were obtained by adding approximately 0.01 g. of various chlorides to a reaction mixture containing 0.06 mole of the alkyl halide and 1.7 g. of a 12% copper–magnesium alloy: cyclohexyl bromide with ferric chloride, −29%; with aluminum chloride, −13%; with mercuric bromide, −17%; with zinc chloride, −32%; benzyl chloride with ferric chloride, −25%; *n*-butyl bromide with aluminum chloride, −1%; with magnesium bromide, +1%; with zinc chloride, −21%. [b] These figures represent the differences in percentage between the values given in columns 2 and 3 of this table, and the values given in Table I for the yield of Grignard reagent and R_2Mg obtained in the absence of mercuric chloride or zinc. [c] There is a change of several per cent. in the value when the solution is allowed to stand for from one to twenty-three hours. The percentage of R_2Mg increases and the amount of halogen in the solution decreases, due no doubt to the precipitation of $MgCl_2$. This is in agreement with Schlenk, *Ber.*, **64**, 734 (1931). [d] 0.2–0.4 g. of zinc, 6.5 g. of magnesium, 0.06 mole of alkyl halide. [e] 0.2 g. of zinc, 1.53 g. of magnesium and 0.06 mole of alkyl halide. [f] 0.2 g. of zinc, 4.0 g. of magnesium, 0.06 mole of alkyl halide. [g] 0.04 g. of mercuric chloride, 1.53 g. of magnesium and 0.06 mole of alkyl halide. [h] 0.04 g. of mercuric chloride, 1.53 g. of magnesium in an 88% magnesium–12% copper alloy, and 0.06 mole of alkyl halide.

curic chloride in some cases markedly increased the yield of Grignard reagent while with other halides the effect was the more normal one for metallic chlorides, *i. e.*, it decreased the yield. Both copper and mercuric chloride affected the proportion of Grignard reagent existing as R_2Mg. With mercuric chloride the effect upon the yield of Grignard reagent for a given alkyl halide was the same as it was upon the proportion of R_2Mg, *i. e.*, both were increased or both were decreased.

Conclusions and Summary

The yields of Grignard reagent and the proportion of dialkyl magnesium (R_2Mg) contained in each of them, as conditioned by the presence of copper, mercuric chloride, etc., have been ascertained for sixteen alkyl halides. The results so obtained and other data on certain related reactions seem to lead to the following conclusions.

1. The proportion of Wurtz and Grignard reactions which occur when an alkyl halide reacts with magnesium varies with the particular alkyl group and the halogen involved. It is also modified by the presence in the reaction mixture of small amounts of the metals copper and zinc and of mercuric and other metallic halides. The effect of copper, for example, upon the proportion of the two competitive reactions is not fixed but varies both in amount and in direction of change. For example, copper *decreased* the Grignard reaction from 72 to 6% for allyl bromide and *increased* the same reaction with *tert.*-butyl chloride from 28 to 43%.

2. The proportion of the active Grignard reagent existing as R_2Mg varies with the alkyl halide from which it is prepared, the variation being from 6% for ethyl iodide to 84% with *n*-butyl chloride. The proportion of R_2Mg is also modified by the presence of copper, mercuric chloride, etc., the variation being from a decrease of 21% in R_2Mg for benzyl bromide to an increase of 13% of R_2Mg from *tert.*-butyl chloride.

3. Those added reagents which for a given alkyl halide decrease the yield of Grignard reagent also in general decrease the proportion of the reagent existing as R_2Mg, and those reagents which for a given alkyl halide increase the yield of Grignard reagent also increase the proportion of R_2Mg in that reagent.

4. The alkyl halides except allyl bromide were quite inactive toward the Grignard reagent made from them (and also toward the R_2Mg component of that reagent) under the conditions under which the reagent is formed. It seems very improbable, therefore, that the formation of hydrocarbons (Wurtz reaction) during the reaction of magnesium with alkyl halides is dependent upon the reaction of the Grignard reagent with the alkyl halide.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE CONSTITUTION OF ABNORMAL AMMONIUM SALTS[1]

BY W. H. HUNTER AND GORDON D. BYRKIT

RECEIVED NOVEMBER 23, 1931 PUBLISHED MAY 7, 1932

Investigations of the systems in which abnormal ammonium salts are reported to exist are far from numerous. Kuriloff[2] studied the system, ammonium nitrate–hydrogen nitrate, and showed that the only abnormal compound was $HNO_3 \cdot 4NH_3$. Kendall and Davidson[3] investigated the systems of ammonia with halogen hydrides, and demonstrated the existence of the compounds $HX \cdot 4NH_3$ in which X is chlorine, bromine and iodine and also the compound $HI.5NH_3$. These authors state that the compounds of the types $HX \cdot 2NH_3$ and $HX \cdot 7NH_3$ reported by Troost[4] do not exist. They found no abnormal compounds in the hydrogen fluoride system and no compounds in any of these systems in which the ratio of acid to base was greater than one.

While there are, apparently, no investigations of the systems of amines with halogen hydrides,[5] there are numerous compounds in the literature which belong to these systems. The compounds reported by Berliner and Hann[6] of the type Base·4HF are especially interesting. The bases were aromatic amines of the most diverse sorts. Three of the hydrogen fluoride molecules were "titratable with alkali" while the last was combined as the normal salt of the base. These compounds are all solids and are well characterized by elementary analysis for carbon, nitrogen and fluorine.

Most of the other compounds which are reported in the literature[7] have been reported on the basis of absorption experiments. In general, the method was to pass the anhydrous halogen hydride over the dry normal salt until no further absorption took place at the particular temperature chosen. Kaufler and Kunz,[8] using this method, reported a dihydrochloride

[1] The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Gordon D. Byrkit in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1929. This paper was prepared by the junior author after the death of Dr. W. H. Hunter, which occurred on August 19, 1931. [L. I. SMITH.]

[2] Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).

[3] Kendall and Davidson, THIS JOURNAL, **42**, 1141 (1920).

[4] Troost, *Compt. rend.*, **88**, 578 (1879); *ibid.*, **92**, 715 (1881).

[5] Except that of Leopold [*Z. physik. Chem.*, **71**, 59 (1910)] on the system aniline–hydrogen chloride. This investigation, however, is incomplete in the range 19.6 to 49.7 mole per cent. of aniline, in which abnormal compounds of the type $C_6H_5NH_2 \cdot n$HCl (n = 2, 3 or 4) would occur.

[6] Berliner and Hann, *J. Phys. Chem.*, **32**, 1142 (1928).

[7] Scholl and Escales, *Ber.*, **30**, 3134 (1897); Korczynski, *ibid.*, **41**, 4379 (1908); *ibid.*, **43**, 1820 (1910); Weinland and Reischle, *ibid.*, **41**, 3671 (1908); Weinland and Lewkowitz, *Z. anorg. Chem.*, **45**, 39 (1905); Rohler, *Z. Elektrochem.*, **16**, 431 (1910).

[8] Kaufler and Kunz, *Ber.*, **42**, 385, 2482 (1909).

of dimethylamine, liquid di- and trihydrochlorides of trimethylamine and also reported that methylammonium chloride absorbed no hydrogen chloride. This is a series of abnormal compounds in which the maximum number of halogen hydride molecules added is equal to the number of alkyl groups in the amine. The influence of alkyl groups in this case would constitute an exception to the usual view, since the effect of the type and number of alkyl (and aryl) groups on the character of the ammonium salts formed is usually very small with respect to all other properties. Except for the work of Wieland[9] and Rheinboldt,[10] who showed that the number of molecules of desoxycholic and other bile acids[11] which added to one molecule of fatty acids, esters, etc., was directly dependent on the number of methyl and methylene groups in the molecule, there seems to be no work indicating a relation between the size and character of alkyl groups and the additive power of the molecule.

Experimental Method

The purposes of the present investigation were two: first, to determine whether or not the compounds reported by Kaufler and Kunz exist, and, second, to investigate further the systems obtained from amines and halogen hydrides, in order to ascertain whether there is a discoverable relation between the number and nature of the groups in a substituted ammonia and the amount of halogen hydride which may be added to it. Two types of measurements accordingly were made. We determined the amounts of halogen hydride absorbed by the amines at various temperatures, and also investigated the thermal behaviors of the systems thus formed.

Preparation of Materials

Dimethylammonium Chloride.—Kahlbaum's liquid dimethylamine was dissolved in ice cold toluene and dry hydrogen chloride passed into the cold solution until precipitation was complete. The crystals were filtered off, washed with dry benzene and dried; m. p. 167°.

Trimethylammonium Chloride.—This was prepared by students from ammonium chloride and paraformaldehyde. A solution of this material was made strongly alkaline, the base distilled into concentrated hydrochloric acid and the salt crystallized out. The process was repeated and the salt recrystallized several times from water, finally being dried over anhydrous calcium chloride in a desiccator; m. p. 273–275°, with decomposition.

Tetramethylammonium Chloride.—This was prepared by dissolving dry trimethylamine in purified methanol and saturating this solution with methyl chloride. The solution was concentrated to crystallization and the product recrystallized from methanol. The salt was treated with silver oxide in aqueous solution and, on crystallizing it

[9] Wieland and Weil, *Z. physiol. Chem.*, **80**, 287 (1912); Wieland and Sorge, *ibid.*, **97**, 1 (1916); Wieland, *Z. angew. Chem.*, **42**, 421 (1929).

[10] Rheinboldt, *ibid.*, **37**, 834 (1924); Rheinboldt, Pieper and Zervas, *Ann.*, **451**, 256 (1926); Rheinboldt, König and Otten, *ibid.*, **473**, 249 (1929).

[11] Boedecker, *Ber.*, **53**, 1853 (1920).

from methanol, a product was obtained which gave no odor of trimethylamine with aqueous alkali.

Methylphenylammonium Chloride.—Vacuum distilled methylaniline was dissolved in dry toluene and dry hydrogen chloride passed in to complete precipitation. The salt was filtered off, washed with dry benzene, dried and recrystallized from purified acetonitrile; m. p. 123.7–124.2°.

Absorption Experiments

Dry hydrogen chloride was passed over a weighed quantity of the normal salt in a weighed absorption bulb placed in a constant temperature bath until no more absorption took place. The increase in weight is the amount of hydrogen chloride absorbed by the salt. Results, expressed as the ratio of moles of hydrogen chloride to moles of base in the saturated mixture at various temperatures, are given in Table I. In most cases the resulting product was liquid.

TABLE I

ABSORPTION OF HYDROGEN CHLORIDE BY AMINES AT VARIOUS TEMPERATURES

Temp., °C.	Moles HCl / Moles Me_2NH	Moles HCl / Moles Me_3N	Moles HCl / Moles Me_4NCl	Moles HCl / Moles MePhNH
31.8		2.41		
Room				1.928
24.0		2.50		
21.9		2.48		
0.0		2.99	1.079	
− 3.6	2.45			
−13.1			1.181	
−21.8		3.81		
−22.0		3.82		
−24.7[a]		4.02		
−24.8[a]		3.95		

[a] It was difficult to maintain these low temperatures constant, hence the variation in results.

Discussion of the Absorption Experiments

The data in Table I show that the amount of absorption of hydrogen chloride by the normal salts depends on the temperature; as this is lowered, the amount of absorption increases. It is true as Kaufler and Kunz state that trimethylammonium chloride absorbs two additional moles of the gas at 0°. However, since the amount of absorption shows a continuous change, so that any ratio whatever may be obtained by a proper choice of temperature, it appears that the report of the compound $(CH_3)_3N\cdot 3HCl$ is erroneous. The same authors report a dihydrochloride of dimethylamine on the basis of the amount of hydrogen chloride absorbed by the normal salt at ordinary temperatures.[12] This again seems to be a fortuitous choice

[12] Their statement[8] "0.1624 g. Dimethylaminhydrochlorid nahmen bei gewöhnlicher Temperatur 0.971g. Chlorwasserstoff auf = 1.00 Mol HCl," however, is erroneous either in data or calculation. The data given correspond to the absorption of 13.26 moles of hydrogen chloride by the normal salt.

of temperature since at $-3.6°$ the normal salt absorbs 1.45 moles of hydrogen chloride or a total of 2.45 moles per mole of base.

Other salts as well show a non-stoichiometric absorption of hydrogen chloride at various temperatures. In such experiments as these we seem to be determining the solubility of hydrogen chloride in the liquid phase present, and this changes gradually with the temperature without reference to the stoichiometric relation between the two components. *At the same time, there is a strong force acting between many of these normal salts and hydrogen chloride.* Trimethylammonium chloride, especially, absorbs the gas with an avidity which is comparable only with the absorption of water vapor by potassium hydroxide.

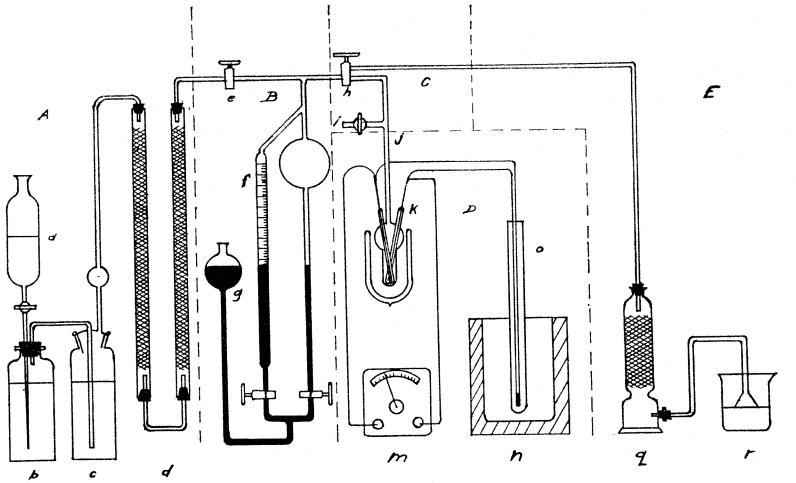


Fig. 1.

Thermal Investigation

Preparation of the Mixture.—The apparatus shown in Fig. 1 was used. The thermocouple tube, k, was first weighed, filled with pure normal salt,[13] reweighed and sealed to the apparatus at j. Hydrogen chloride was generated in b. After passing through the bubbler of concentrated sulfuric acid, c, the gas continued through two long tubes, d, packed with anhydrous calcium chloride to remove oxides of sulfur. With both the buret and bulb filled with mercury and stopcock h opened to E, the system was flushed with hydrogen chloride until all the air was removed, while a water pump attached at i removed the air from the thermocouple tube. With h closed and the buret, f, filled with mercury, the calibrated bulb of five hundred cubic centimeters' capacity was filled with hydrogen chloride to the lower mark. With stopcocks e and i closed, h was opened to the bulb, k, which was surrounded by a Dewar flask of liquid air. Hydrogen chloride was condensed into k until when the stopcock, h, was closed and the mercury leveled, it stood at the upper mark of the calibrated bulb. The temperature and pressure were noted during this process. By using the bulb and/or buret (for quantities less than 500

[13] On account of the great hygroscopicity of these salts, this operation was accomplished in a desiccator box.

cubic centimeters) any desired quantity of hydrogen chloride could be condensed into k, resulting in a mixture of any desired composition.

Melting Point Determination.—With stopcock h closed, the tube k was surrounded by liquid air until all of the hydrogen chloride had been condensed (five minutes was sufficient). Stopcock i was opened to the air,[14] and the tube sealed off at j. The tube was then warmed until the contents were melted and thoroughly mixed. The thermocouple tube was air jacketed and fitted with the wires of the cold junction of the thermocouple while the hot junction was placed in a stirred bath of ice and water. The jacketed tube was surrounded by a cooling bath about 20° below the approximate freezing point of the mixture, and the millivoltmeter (calibrated at the freezing point of several highly purified organic liquids) was read at regular intervals. The horizontal portion of the cooling curve thus obtained represented the freezing (melting) point of the mixture and the corresponding temperature was read from the calibration chart of the thermocouple.

In cases in which the melting point of the mixture was near or above 0°, a tube without provision for the thermocouple junctions replaced k. The procedure for the preparation of the sample was precisely the same. The melting points were determined by placing the sealed tube in a stirred glycerin bath which was warmed very slowly. Several determinations, at twenty-four hour intervals, were made on each tube. The necessity for the long interval between determinations is, of course, the fact that as the temperature is raised to the melting point, hydrogen chloride passes into the vapor phase, which changes the melting point. More consistent results were therefore obtained if the contents of the tubes were allowed to return to equilibrium before a second determination was made.

The systems trimethylamine– and methylphenylamine–hydrogen chloride were investigated in this way. The results are given in Tables II and III and the corresponding Figs. 2 and 3.

TABLE II

THERMAL DATA ON THE SYSTEM TRIMETHYLAMINE–HYDROGEN CHLORIDE

Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.
55.4	270 dec.	66.6	56.3	72.5	−54.5
56.7	260 dec.	67.1	49.1	74.0	−87.3
59.6	199.6	68.1	15.4	75.0	−126.8
60.5	125–130	69.1	− 1.4	76.6	−126.0
65.3	62.9	72.4	−54.5	78.1	−116.3

TABLE III

THERMAL DATA ON THE SYSTEM METHYLPHENYLAMINE–HYDROGEN CHLORIDE

Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.
60.10	79.5	66.99	36.4	72.95	34.0
61.99	55.4	67.50	36.6	75.37	31.2
63.36	38.4	68.03	34.8	77.48	20.9
63.96	32.8	68.39	38.4	80.22	1.3
64.48	33.7	68.94	36.8	81.53	−17
65.21	34.6	69.07	36.7	82.11	< −24
65.74	34.9	69.52	38.4	84.96	< −24
66.45	37.6	70.15	37.6		

[14] When a tube prepared as described and surrounded by liquid air for five minutes was broken off at j and held at the mouth of a bottle of 28% *ammonia*, no fumes were formed; hence there was no loss of hydrogen chloride.

Investigations in the systems methylamine- and dimethylphenylamine–hydrogen chloride offered considerable difficulty and were finally laid aside. In the first case, the normal salt seemed to have no tendency to absorb hydrogen chloride and the pressures developed on warming were almost invariably greater than the glass tubes would stand. In the second case, the normal salt was too hygroscopic to be handled even in the desiccator box. Attempts to use the free base were also unsuccessful because of the high melting point of dimethylaniline (2°) which prevented the base from reacting with the hydrogen chloride as it was condensed into the bulb. Before the base was warm enough to react, the pressure of the hydrogen chloride was always sufficient to break the tube.

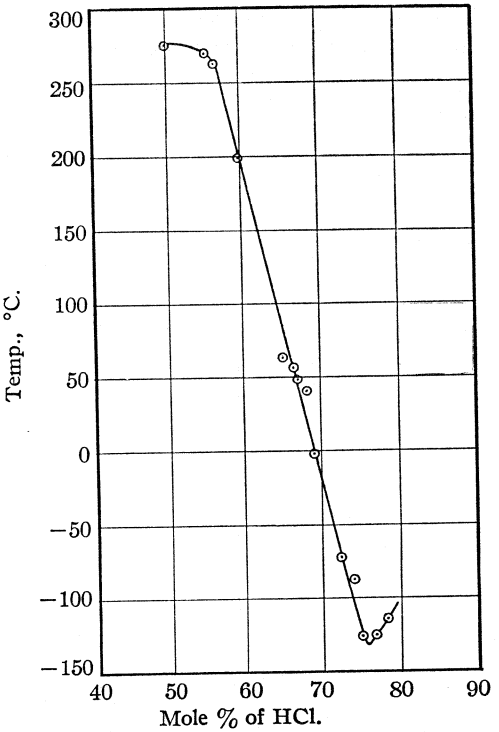


Fig. 2.—Trimethylamine–hydrogen chloride.

Discussion of Thermal Investigations

That di- and trihydrochlorides of trimethylamine do not exist is evident from the thermal diagram of the system (Fig. 2), since there are no maxima at either $66^2/_3$ or 75 mole per cent. of hydrogen chloride. On the other hand, it is equally evident from Fig. 3 that a dihydrochloride of methylaniline is formed. That the high point of the curve is at 69 mole per cent. hydrogen chloride rather than at $66^2/_3\%$ is to be expected because at the temperatures at which these mixtures melted, much of the hydrogen chloride was in the vapor phase. Thus, while sufficient gas had been placed in the tube to give a mixture of the composition 69% hydrogen chloride, enough was probably in the vapor phase and therefore without effect on the melting point, to reduce the amount in the solid and liquid phases to $66^2/_3\%$.[15]

[15] In general, the melting points below −83° (the boiling point of hydrogen chloride) are the most accurate. As the temperature of fusion rises, the observed melting points become higher and higher than they would be were all the hydrogen chloride in the solid and liquid phases. This accounts for the extreme flatness of the curves in the neighborhood of the normal salt.

A General System of Molecular Compounds of Higher Order

Werner's[16] formulation of normal and abnormal ammonium salts as $[H_3N....H]X$ and $[H_3N....H....NH_3]X$, respectively, is usually extended in the case of abnormal salts with extra ("exo")[17] *acid* molecules by assuming the addition of the exo molecules to the anion of the salt, thus

$$\begin{bmatrix} R. & .R \\ & .N. \\ R & R \end{bmatrix}\begin{bmatrix} X...HX \end{bmatrix}; \quad \begin{bmatrix} R. & .H \\ & .N. \\ R & H \end{bmatrix}\begin{bmatrix} & .HX \\ X. & \\ & HX \end{bmatrix}; \text{ etc.}$$

However, these formulas do not express experimental facts in that, while ammonium chloride does not add hydrogen chloride,[18] many substituted

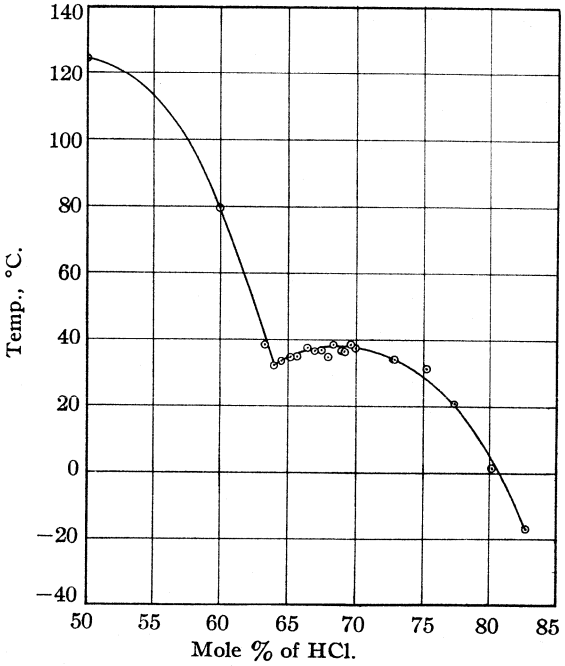


Fig. 3.—Methylphenylamine–hydrogen chloride.

ammonium chlorides do. Since the difference here is in the character of the cation of the salt, formulas for dihydrochlorides, etc., must be based on the cation of the salt, and must not involve the anionic chlorine, which is identical in both cases.

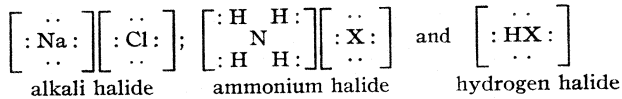
The attempt to correlate the additive properties with the change in character of the cation depends on a development of the conception of

[16] Werner–Pfeiffer, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," fifth edition, Braunschweig, 1923.

[17] Werner–Pfeiffer, Ref. 16, p. 310; Weinland, "Einführung in die Chemie der Komplex-Verbindungen," second edition, Stuttgart, 1924, p. 327.

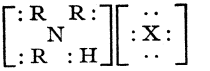
[18] Kendall and Davidson, THIS JOURNAL, **42**, 1141 (1920).

"pseudo atoms" of Grimm[19] and Glockler.[20] According to these authors, the well-known similarity of the ammonium and potassium ions, the former a pseudo atom of neon and the latter of argon, lies in that the L electrons of the nitrogen atom are so altered by the sphere of four protons (which are *inside* their respective electron pairs in the ammonium ion) that they behave almost as the M electrons of the potassium ion. That neither the alkali halides nor ammonium halides add halogen hydrides, as Kendall and Davidson[3] observed, is not surprising when their electronic structure is considered



In the terminology of Sidgwick,[21] these are all donors.

However, substituted ammonium halides do absorb halogen hydride even when there is no formation of definite compounds. It is conceivable that in these the alkyl and aryl groups are of such size that in replacing the protons they so distort the electronic arrangement of the atom that some or all of the remaining protons lie without the L shell, thus



With such a configuration as this, it is possible that the protons so "extrapolated" may possess the power of coördination in quite a weakened sense. It is possible to account on this basis for the absorption of hydrogen chloride, for example, by trimethylammonium chloride, even though the additive power of the extrapolated proton is insufficient to cause the formation of a definite compound. With methylphenylammonium chloride, on the other hand, the comparatively great size of the phenyl group, together with the methyl group, makes this extrapolation so pronounced that a definite compound, $CH_3(C_6H_5)NH\cdot 2HCl$, is formed. The exo molecule is bound in the "second sphere" of Werner,[22] the substituted ammonium ion acting as the center of the complex. It is possible to conceive of a third zone in which the forces available to bind additional molecules are much weaker than those of the second sphere, and may even attract molecules without binding them in a stoichiometric way.

No matter how they may be written in a Werner type formula, it seems of great importance that these compounds with exo molecules form a transition from the coördination compounds of Werner, in which groups of definite number are geometrically arranged about a central atom, to the "ion atmosphere" of Debye and Hückel, in which there is an indefinite

[19] Grimm, *Z. Elektrochem.*, **31**, 474 (1925).

[20] Glockler, THIS JOURNAL, **48**, 2021 (1926).

[21] Sidgwick, "Electronic Theory of Valency," Oxford University Press, 1927.

[22] Werner–Pfeiffer, Ref. 16, p. 234.

"cloud" of electrostatically attracted dipole molecules or ions about another ion or about another strongly dipolar molecule. These forces are often considered to be all of the same nature, that is, electrostatic,[23] and it is on this basis that an organization of our knowledge is possible with the aid of Table IV. In the compounds of the first and second orders, the groups about the central atom, which are definite in number and position in the molecule, are held by the strong forces of primary valence in the first-order compounds and by the weaker forces of secondary valence in the second-order compounds. Intermediate between these two types are the compounds in which, while the number and position of the groups about the central atom are definite, it is difficult to say whether the groups are held by primary or secondary valence. The nitroprussides, metal carbonyls, etc., are examples.

Compounds of the third order are those in which, while the number of added molecules is stoichiometric, it is at present impossible to determine the exact arrangement of the constituents of the molecule, as in many dihydrochlorides of monacid ammonium bases. Between the second and third orders are those compounds formed by addition to molecules already coördinatively saturated, as, for example, $NiCl_2 \cdot 8NH_3$.

Those compounds in which the number of bound molecules is indefinite even though there is marked affinity between the two components (for example, trimethylammonium chloride and hydrogen chloride) lie between the compounds of the third order and the class of Debye and Hückel. In the latter there is an indefinite cloud of dipoles, which may be either oppositely charged ions or neutral molecules, about a central dipole, which again may be either an ion or a molecule. The exo compounds in which we have been especially interested include compounds of the third order and the intermediate types on both sides.

TABLE IV

COMPOUNDS OF HIGHER ORDERS

Order	First	Second	Third	Debye-Hückel
Type compounds	CCl_4	$[Co(NH_3)_6]^{+3}$	[MePhNH.2HCl]	$[K^+(Cl^-)n]$
Intermediate types	$[Fe(CN)_5(NO)]^{-4}$	$NiCl_2.8NH_3$	$Me_3NHCl + HCl$	
Number of groups	Definite	Definite	Definite	Indefinite
Location of groups	Definite	Definite	Indefinite	Indefinite
Strength of binding	Strongest ---->	Decreases ---------->		Weakest
		<---- Exo compounds ---->		

Summary

1. It has been shown that di- and trihydrochlorides of trimethylamine do not exist. This is another example of the fallacy of assuming the

[23] Magnus, *Z. anorg. allgem. Chem.*, **124**, 289 (1922); van Arkel and de Boer, *Rec. trav. chim.*, **47**, 593 (1928). Compare also the cluster theory of gas reactions of Lind ["Chemical Effects of Alpha Particles and Electrons," New York, 1928].

existence of abnormal compounds on the basis of absorption experiments only.

2. The existence of a dihydrochloride of methylaniline has been shown by means of a thermal diagram of the system.

3. An explanation of the absorption of hydrogen chloride by the normal ammonium salts with and without the formation of stoichiometric compounds has been advanced.

4. An attempt has been made to bring all molecular compounds of higher orders into one general system.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

AN IMPROVED PROCEDURE FOR THE PREPARATION OF ORGANOLITHIUM COMPOUNDS

BY HENRY GILMAN, E. A. ZOELLNER AND W. M. SELBY

RECEIVED DECEMBER 4, 1931 PUBLISHED MAY 7, 1932

Introduction

The chief and outstanding chemical difference between organometallic compounds containing alkali metals and those prepared from alkaline earth metals is the general tendency of the former to add to some ethylenic linkages and the absence of such addition with organometallic compounds like the Grignard reagent. There are, of course, occasional differences in a series of organolithium compounds, for example, just as there are differences between RMgX compounds. It is reasonable to expect that, in general, the mechanisms of reaction of these two groups of organometallic compounds with a given reactant would be similar and, in many cases, identical. However, the literature contains numerous cases where the mechanism proposed with organoalkali compounds does not agree with that established with organomagnesium compounds. It was in connection with such studies, as they concern terminal cumulated unsaturated linkages and allylic systems, that we needed phenyl-lithium in quantity.

Organolithium compounds were first prepared by Schlenk and Holtz[1] by the reaction of lithium with an R_2Hg compound in accordance with this general reaction, which has recently been shown to be reversible[2]

$$R_2Hg + Li \longrightarrow 2RLi + Hg \qquad (I)$$

The technique in this operation was subsequently improved and excellent

[1] Schlenk and Holtz, *Ber.*, **50**, 272 (1917). See, also, Groll, THIS JOURNAL, **52**, 2998 (1930).

[2] Ziegler and Colonius, *Ann.*, **479**, 135 (1930). For other studies on the reaction between RX compounds and lithium, see Spencer and Price, *J. Chem. Soc.*, **97**, 385 (1910), and Wittig and Leo, *Ber.*, **64**, 2395, 2405 (1930).

yields of alkyl-lithium compounds were obtained more conveniently.[3] More recently, the elegant studies by Ziegler and Colonius[2] have shown that it is possible to prepare many organolithium compounds by the direct interaction of lithium with an RX compound in ether or benzene, the latter solvent being preferred with alkyl-lithium compounds because they react much more rapidly with ether than do aryl-lithium compounds.

$$RX + 2Li \longrightarrow RLi + LiX \qquad (II)$$

An essential and long-practiced difference in manipulation of organoalkali compounds and compounds like Grignard reagents lies in the use of glass-sealed containers of various modifications for the preparation and subsequent reactions of the organoalkali compounds. The purpose of the sealed containers is to exclude rigidly the deleterious effects of the atmosphere and moisture. However, because RMgX compounds are also sensitive to moisture, oxygen and carbon dioxide and yet can be prepared and manipulated very satisfactorily with a minimum of refinements to diminish the destructive action of moist atmosphere, it occurred to us that a corresponding simpler technique might be used with organoalkali compounds like phenyl-lithium, etc.

This finds support in experiment. Phenyl-lithium, for example, can be prepared very readily and in excellent yields from lithium and bromobenzene in ether. The general manipulation is that used in the preparation of Grignard reagents. Actually, the 95% yield of phenyl-lithium, obtained about as rapidly as the usual 95% yield of phenylmagnesium bromide, is 15–25% in excess of that reported recently.[2] The yields were determined by the acid-titration method of analysis used in studies on organomagnesium compounds. As a check on this analytical procedure, the phenyl-lithium was treated with an equivalent of benzophenone and the yield of triphenylcarbinol obtained in this manner was essentially that expected. For this reason, it was considered unnecessary to use also the *n*-butyl bromide–dibenzylmercury indirect method of analysis.[2]

The yield of phenyl-lithium from iodobenzene, lithium and ether was 80%. The yield of phenylmagnesium iodide prepared under corresponding conditions is 85.6%. There is then a resemblance in the effect of various phenyl halides on the yields of phenyl-lithium, and of phenylmagnesium bromide and phenylmagnesium iodide. However, this correlation breaks down apparently when the yields are compared in corresponding experiments where the phenyl halide is added very rapidly to the metal in ether. When bromobenzene is added rapidly to magnesium in ether the yield is 89.8%, or a drop of 4.9% from that obtained under "normal" conditions. With phenyl-lithium prepared by the rapid addition of bromobenzene the drop in yield is of the same order, namely, 3.9%. But with phenyl-

[3] Hager with Marvel, THIS JOURNAL, **48**, 2689 (1926). The latest paper by Marvel and co-workers with organolithium compounds is *ibid.*, **52**, 376 (1930).

lithium prepared by the rapid addition of iodobenzene, there is no drop in yield, whereas the rapid addition of iodobenzene to magnesium in ether gives a 71.8% yield of phenylmagnesium iodide, or a drop of 13.8%.

It might have been predicted that the rapid addition of *n*-butyl chloride to lithium would not decrease the yield, because the 91.9% yield of *n*-butylmagnesium chloride obtained under so-called normal conditions is not decreased by a rapid addition of the halide. This prediction is supported by experiment, and there is no essential drop in yield with the rapid addition of *n*-butyl chloride to lithium in ether. The reaction between lithium and *n*-butyl chloride in benzene is slow,[2] and under our conditions the yield of *n*-butyl-lithium after six hours is 70%. However, the formation of *n*-butyl-lithium in ether is more rapid and yields of 75–80% are readily obtained. No study was made of the optimal conditions for the preparation of *n*-butyl-lithium since our prime need was phenyl-lithium.

The practical significance of the observation that there is no appreciable drop in yields in the preparation of phenyl-lithium and *n*-butyl-lithium lies in the fact that these organolithium compounds can be prepared conveniently without regard to the rate of addition of halide. If analogies between organometallic compounds prepared from alkali metals and alkaline earth metals have any significance, then it is probable that the yields of other organolithium compounds will vary with the rate of addition.[4] This is based on published studies on the preparation of such Grignard reagents as allylmagnesium bromide, *tert.*-butylmagnesium chloride, cinnamylmagnesium chloride, etc.

The advantages of manipulating organolithium compounds in either open containers, or with a slow stream of nitrogen in essentially open containers, provided with the conventional mercury-sealed stirrers, will undoubtedly apply with other organoalkali compounds. A case in point is the addition of sodium to benzophenone-anil and the subsequent carbonation of the di-sodium compound, $(C_6H_5)_2C(Na)N(Na)C_6H_5$, to give ultimately diphenylanilinoacetic acid, $(C_6H_5)_2C(NHC_6H_5)COOH$, in practically quantitative yields.[5] It is significant that carbon dioxide, one of the atmospheric constituents that has a deleterious effect on reactive organometallic compounds, reacts with phenyl-lithium to give a very poor yield[2] of benzoic acid. This is in striking contrast with RMgX compounds which generally give very high yields of carboxylic acids.[6] Oxygen with phenyl-

[4] Another important factor is the excess of lithium used. An excess of lithium has no effect[2] on the yields of organolithium compounds mentioned in this paper. An excess of magnesium is very helpful in obtaining high yields of RMgX compounds like allylmagnesium bromide, etc.

[5] Studies by Mr. R. H. Kirby. The original reaction was carried out by Schlenk and Michael, *Ber.*, **47**, 483 (1914).

[6] The only two exceptions in our experience are with the carbonation of allylmagnesium bromide and β-styrylmagnesium bromide.

lithium, as with phenylmagnesium halides, induces chemiluminescence. In these incidental studies the color test for reactive organometallic compounds has been found to be highly useful to determine whether an organolithium compound was formed, and when it was used up in a given reaction. In reactions with ketones, it appears that any unused lithium might act as an indicator by developing distinctive colors (possibly those of ketyls) when the ketone is used up in its reaction with the organolithium compound. For example, in a preparation of triphenylcarbinol from benzophenone and phenyl-lithium, when the phenyl-lithium was used up (as indicated by a negative color test), a violet color developed near some small pieces of unused lithium which had not been removed. Characteristic colors were also observed when the ether solution of *n*-butyl-lithium was treated with α-naphthyl isocyanate in the preparation of *n*-valero-α-naphthalide as a derivative.

Experimental Part

The apparatus and general procedure were those used in related studies on organomagnesium compounds. Some modifications, concerned largely with the cutting of lithium, used in the small quantitative studies are unnecessary in the preparation of phenyl-lithium and *n*-butyl-lithium in large quantities. A few details of the small-sized quantitative experiments are given because they serve to correlate the present procedure with that of organomagnesium halides, and because they may prove of assistance to others in not only determining optimal conditions for some organolithium compounds which cannot now be prepared satisfactorily, but also in determining the relative labilities of halogens in RX compounds toward various metals.

The small quantitative studies were all carried out in a nitrogen atmosphere for two reasons. First, organolithium compounds undergo ready reaction with oxygen. Second, the purity of RX compounds appears to have a greater influence on initiating reaction with lithium than with magnesium. In larger runs it may be unnecessary to use a nitrogen atmosphere with most aryl halides. Such an atmosphere is necessary with a slow reacting compound like chlorobenzene and with the alkyl halides, in order to reduce appreciable decomposition due to the diffusion of atmospheric oxygen.

The metal was cut by means of a chisel and hammer into pieces measuring about 7 × 7 mm. in cross section and 30 mm. in length. These were shaped into prisms of about the above-mentioned dimensions by means of pliers having smooth-faced jaws, and this operation apparently served to press out most of the kerosene under which the original metal was kept. Incidentally, the lithium prisms were shaped fairly uniformly to ensure an approximately constant thin oxide layer. These prisms were readily scraped and cut so that they weighed 0.76 g. (1.1 atoms), the quantity used in the 0.05 mole experiments, allowing a 10% excess. They were then kept, for a few minutes prior to use, under dry ether in an inverted test-tube arrangement provided with a small hole near its upper end to permit escape of any entrapped air. The ether level was over this orifice in the test-tube, and a handle made it convenient to remove the tube from the Erlenmeyer flask in which it was contained.

The simplified, analytical reaction flask used in organomagnesium studies was heated in an oven at 110°, and swept out with pure, dry nitrogen which was admitted through the side neck. After adding 15 cc. of ether, the prism of lithium was cut transversely (by means of a scissors) into about thirty pieces which were allowed to drop into the flask through the main neck, from which issued a stream of nitrogen.

The flask was then attached to the mercury-sealed stirrer (fitting the main neck) and dropping funnel which entered the main neck through a second boring in the rubber stopper holding the stirrer, and a spiral condenser (fitting the side neck). The top of the spiral condenser and the top of the dropping funnel were connected by tubes provided with pinchcocks which made it possible to admit nitrogen through the condenser or (and) through the dropping funnel. The nitrogen now left the system through a U-tube having a 2–3 mm. head of mercury pressure. This gage permitted the subsequent operations with a minimum actual flow of nitrogen, and very little loss of ether.[7]

Then 40 drops of the halide was added to the lithium and ether. Gentle warming by means of a micro-burner was sufficient to induce prompt reaction. Reaction having set in, the remainder of the halide in 15 cc. of ether was added either over a period of thirty to thirty-five minutes in a so-called normal run or all at once in those experiments concerned with the effect of rapid addition on the yield. Stirring was used throughout the preparation.

When the preparation was completed, the flask containing nitrogen was detached from the rest of the apparatus, stoppered and allowed to stand for thirty minutes, at the end of which time any precipitate settled. The visible unused lithium was readily removed by long-handled tweezers, and aliquots were taken for analysis.[8] As in related quantitative studies with organomagnesium compounds, each of the experiments was checked at least twice and the degree of accuracy for aliquots from a given preparation is that obtained with Grignard reagents.

Miscellaneous Observations

Size of Lithium.—When the 0.76 g. prism of lithium was cut lengthwise into two pieces, the yield of phenyl-lithium from bromobenzene was 93.1%. In this experiment, the apparent reaction continued for fifty to fifty-five minutes; whereas under standard conditions with smaller pieces of lithium the apparent reaction continued for ten to twenty minutes. The mixture was then refluxed for an additional forty-five minutes. For practical purposes it is, therefore, unnecessary to cut the lithium into small pieces if the slightly greater time required for completion of the reaction is of secondary consequence.

Tarnishing of Lithium.—In one experiment with lithium and bromobenzene, the 30–33 pieces of metal (totaling 0.76 g.) were exposed to moist air for one minute, which was sufficient to coat them entirely with a black film. Reaction set in at once, probably because the sharp-winged small stirrer removed some of the oxide, as was evidenced by the clean, silvery patches on the metal after stirring for a few minutes. The yield of phenyl-lithium was 86.8%. It is possible that an adequate excess of tarnished metal may prevent a decrease in yield. When one piece (0.76 g.) of tarnished lithium was used, the yield was 88.6%, and about five minutes of stirring with the application of heat was required for the starting of reaction. Stirring was obviously less effective with the single piece of lithium in the small flask.

Time of Reaction.—In every case it appears desirable to apply heat and to use stirring in initiating reaction. With Grignard reagents it is generally better not to use stirring until after the reaction has commenced. The time of apparent reaction, after all of the halide had been added very rapidly (in so-called drop runs) to the lithium in ether, varies with the RX compound and is probably a measure of the labiltiy of the halogen toward a given metal. With iodobenzene this time is ten to fifteen minutes;

[7] In large-sized runs, particularly with slow acting RX compounds, it may be sufficient to use a trap to exclude the atmosphere subsequent to sweeping out the apparatus with nitrogen.

[8] During these operations, nitrogen was admitted through the side neck.

with bromobenzene, thirty-five to forty minutes; and with *n*-butyl chloride, forty to forty-five minutes. The corresponding times when these halides are added separately to magnesium in ether are: ten to fifteen minutes; ten to fifteen minutes; and forty-five to fifty minutes, respectively.

When the apparent reaction is ended, refluxing with stirring should be continued for forty-five minutes. There is no improvement in yield of phenyl-lithium from bromobenzene when this period of refluxing exceeds thirty minutes; and with a fifteen minute period of refluxing the yield was 92%.

Yields of Some Other Aryl-lithium Compounds.—Under corresponding conditions the following yields were determined from RBr compounds, the number in parentheses being the percentage yield when the RBr compound was added rapidly to the lithium: *o*-tolyl-lithium, 93.3 (85.6); *m*-tolyl-lithium, 86.4 (80.0); *p*-tolyl-lithium, 94.9 (95); *o*-anisyl-lithium, 85 (85); *p*-anisyl-lithium, 66.1 (65.3); α-naphthyl-lithium, 79 (80); and β-naphthyl-lithium 75.3 (47.8).

***n*-Butyl-litihum.**—The time of apparent reaction when all of the *n*-butyl chloride is added to the lithium in ether is forty to forty-five minutes. Gentle refluxing is continued for about two hours, and the yield is 75–80%. In one experiment when the time of refluxing was one-half hour the yield was 67%. When twelve instead of the customary six molecular equivalents of ether were used the yield was 68%. As previously mentioned, the reaction in benzene is much slower than in ether. Because the very high yields of *n*-butyl-lithium in benzene were obtained in twenty-four hours,[2] it may be desirable to prepare *n*-butyl-lithium in benzene in sealed containers; however, effective stirring would probably reduce the time required for complete reaction. The *n*-butyl-lithium was characterized by the preparation of *n*-valero-α-naphthalide from α-naphthyl isocyanate in accordance with the general directions suggested for this reaction in the preparation of derivatives of reactive organometallic compounds. The preparation of *n*-butyl-lithium in ether can be simplified by adding the freshly cut lithium to all of the halide in ether and thereby dispensing with the use of a dropping funnel.

The authors are grateful to Dr. F. Breuer, Dr. B. Barrett Gilman, Mr. E. B. Towne and Mr. P. Van Ess for valuable suggestions and assistance.

Summary

Directions are given for the preparation of aryl-lithiums and *n*-butyl-lithium, from lithium and the corresponding halides. Excellent yields are readily obtainable under conditions essentially like those used with the related Grignard reagents.

Attention is directed to some simplifications in procedure which make it possible to prepare and to manipulate some organoalkali compounds in readily available apparatus and without the use of glass sealed containers.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF BUFFALO]

FURTHER STUDIES IN KETO-ENOL DETERMINATION

BY GLADYS A. MICHALEK AND HOWARD W. POST

RECEIVED DECEMBER 9, 1931 PUBLISHED MAY 7, 1932

Previous work of ours[1] included evidence that ethyl α-phenylacetoacetate exists in the enol form to the extent of about 28.6% at room temperatures. Later work by K. von Auwers[2] presented values of approximately 39.2% for the same property.

We did not find in our first contribution sufficient agreement between bromine titration values representing the enol content of ethyl α-phenylacetoacetate and like figures derived from refractive indices by von Auwers, Brühl or anyone else, in spite of the existence of corrections which might be applied to the latter. It should be noted also that this ester required several days to reach equilibrium after distillation even when the same type of Pyrex glass was used for all operations and for all containers throughout the work.

We have accordingly repeated our work in the hope of being able to reconcile our values with those of von Auwers.

Preparation of the Ester.—Ethyl α-phenylacetoacetate was prepared by the same method outlined in our first paper on this subject. The hydrolysis of acetobenzyl cyanide was, however, modified in that the solution was kept at room temperature instead of at zero degrees during the addition of hydrochloric acid and later was poured into water at room temperature instead of ice water. As in earlier work fractionation was carried out under vacuum using a flask with fractionating column attached. The ester was first collected over a range of fifteen degrees and refractionated to boil at 145–147° under 11 mm. pressure. Two batches of crude ester were purified separately in order to have a check on the index of refraction. Both showed an index of refraction of 1.5130 at 20° when given time to reach equilibrium. Freshly distilled material always showed a high index.

Bromine Titration.—Titration of the enol content was carried out as before. The sample, which was weighed by difference, was introduced into 30 cc. of alcohol at −7° and sufficient freshly prepared alcoholic bromine solution added quickly to give a slight color, which was immediately discharged with alcoholic β-naphthol solution. To this was added 10 cc. of 5% potassium iodide solution and the whole heated on the steam-bath for twenty minutes in the dark, then titrated with $N/10$ sodium thiosulfate solution. The latter had a factor of 1.1227 at 20°. The buret was calibrated and found to be correct at 20° within the accuracy of the titration.

Some trouble was experienced in obtaining β-naphthol sufficiently pure that it could effectively remove the excess of bromine. Distillation of β-naphthol followed by two recrystallizations from water gave a product requiring not more than 0.3 cc. of thiosulfate solution to discharge the color

[1] Post and Michalek, THIS JOURNAL, **52**, 4358 (1930).

[2] Von Auwers, *ibid.*, **53**, 1496 (1931).

of the blank. Calculations were made with and without this correction, however; in the actual titration the amount of thiosulfate accounted for in this way is probably much smaller since the excess of bromine is much less. We know of no way of calculating the actual excess of thiosulfate used in the titration due to the impurity of the β-naphthol. In the previous work a correction of 0.5 cc. was made in the results.

DATA

Temp., °C.	$Na_2S_2O_3$, cc.	Sample, g.	% Enol Titrated	% Enol Corrected
21.5	19.8	0.7353	31.15	30.68
22.0	16.0	.6213	29.76	29.18
22.0	17.9	.6911	29.93	29.44
22.0	13.9	.5256	30.59	29.93
		Average	30.36	29.81

Conclusions.—Our results agree within the limits of experimental error with those of our former paper. In view of the discrepancy still existing between these values and those of von Auwers, we are forced to conclude that the only further light which can be thrown on the question should come from an isolation of enol and keto in the pure state, followed by a determination of the refractive index and the bromine titration value of each.

Summary

The enol content of ethyl α-phenylacetoacetate has been redetermined both by bromine titration and by the determination of the refractive index. The values so obtained check within the limits of experimental error with those previously published by the authors.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

BENZENESULFONYLGUANIDINES[1]

BY H. T. CLARKE AND H. B. GILLESPIE

RECEIVED DECEMBER 10, 1931 PUBLISHED MAY 7, 1932

In the course of an investigation, now in progress, of the benzenesulfonyl derivatives of proteins and peptides, it became necessary to ascertain the effect of benzenesulfonyl chloride upon guanidine and its derivatives under various conditions. Ackermann[2] treated guanidine carbonate with benzenesulfonyl chloride in the presence of excess sodium hydroxide, thereby obtaining the sparingly soluble benzenesulfonylguanidine. He also reported failure to produce a sparingly soluble derivative of arginine under analogous conditions. The corresponding β-naphthalenesulfonyl

[1] Work supported by a research grant from The Chemical Foundation.

[2] Ackermann, *Z. physiol. Chem.*, **47**, 366 (1906).

derivatives of certain guanidines have recently[3] been employed for their characterization in urine.

We have been able to confirm Ackermann's observation with guanidine, but find that the yield of benzenesulfonylguanidine depends upon the amount and the concentration of the sodium hydroxide, as well as upon the amount of benzenesulfonyl chloride employed. The reason for this is not far to seek. Guanidine is a strong base which furnishes a titration curve[4] almost indistinguishable from that obtained with sodium hydroxide, and replacement of a hydrogen atom apparently takes place with guanidine only in its undissociated form.

This view is borne out by the behavior of guanidine carbonate toward benzenesulfonyl chloride in the presence of potassium carbonate, under which conditions the sole product is a well crystalline benzenesulfonate of guanidine.

Analogous results are obtained with methylguanidine, asymmetrical dimethylguanidine and piperidoguanidine, which are bases as strong as guanidine.[4] The resulting benzenesulfonyl derivatives display weakly basic properties, forming crystalline hydrochlorides which appear to be readily hydrolyzed in aqueous solution. Benzenesulfonylguanidine also forms an acetyl derivative and an unstable picrate. It shows no tendency to form salts with alkalies, thereby differing from the majority of primary sulfonamides. This may be interpreted as being due either to the preponderance of the benzenesulfonimino form or, more plausibly, to the inability of the single benzenesulfonyl group entirely to suppress the basic properties of the guanidine molecule. Guanidine nevertheless shows no tendency to form derivatives containing more than one benzenesulfonyl group, nor do the benzenesulfonyl guanidines yield nitrogen by the action of sodium nitrite in presence of acetic acid, therein resembling guanidine.[5]

The guanidine group in arginine appears, from the dissociation curve of arginine[6] and from the fact that benzylidenearginine is incapable of forming a sodium salt,[7] to be as strongly dissociated as guanidine itself. It should therefore be possible, by treating arginine with benzenesulfonyl chloride in the presence of sodium carbonate, to attach a benzenesulfonyl group to the α-nitrogen atom, while leaving the terminal guanidine group untouched. This appears to be the case; monobenzenesulfonylarginine, isolated in the form of its picrate, yields very little nitrogen under the conditions adopted by Van Slyke[5] and must, in consequence, possess the anticipated structure. This is confirmed by the regeneration of the amino group on acid hydrolysis.

[3] Stockholm and Cerecedo, *Proc. Soc. Exptl. Biol. Med.*, **29**, 78 (1931).

[4] Davis and Elderfield, THIS JOURNAL, **54**, 1499 (1932).

[5] Van Slyke, *J. Biol. Chem.*, **9**, 185 (1911).

[6] Foster and Schmidt, *ibid.*, **56**, 551 (1923).

[7] Bergmann and Zervas, *Z. physiol. Chem.*, **152**, 282 (1926); **172**, 277 (1927).

On the other hand, when the benzenesulfonylation is carried out in presence of a large excess of concentrated sodium hydroxide, benzenesulfonyl groups attach themselves to the guanidine group as well. While it was not found possible to isolate the resulting product in crystalline condition, analysis showed it unquestionably to consist of dibenzenesulfonylarginine.

Attempts to prepare benzenesulfonyl derivatives of acetamidine were unsuccessful, benzenesulfonamide being the only product isolated; analogous experiments with creatine also failed.

Experimental

Guanidine Benzenesulfonate.—To a solution of 18 g. of guanidine carbonate (0.2 m. of guanidine) in 125 cc. of water were added 26 cc. (0.2 m.) of benzenesulfonyl chloride and 14 g. (0.2 m.) of potassium carbonate. The mixture was stirred vigorously; the temperature rose to 43°. The crystals which formed on cooling were collected (22 g.) and recrystallized from 50 cc. of water from which they separated in diamond-shaped plates melting at 209–210° (corr.). The product was soluble in nine parts of water at 26°; it was readily soluble in alcohol and insoluble in ether. It could be recrystallized unchanged from dilute sodium hydroxide solution.

Anal. Calcd. for $C_7H_{11}O_3N_3S$: C, 38.7; H, 5.07; N, 19.4; S, 14.8. Found: C, 38.7; H, 5.01; N, 19.0; S, 15.1.

On adding a hot concentrated solution of picric acid to a solution of the salt, guanidine picrate melting at 330° (uncorr.) separated; this picrate contained no sulfur.

Benzenesulfonylguanidine.—Solutions of 3 g. of guanidine carbonate in 35 cc. of water were treated with varying amounts of sodium hydroxide and 6-cc. quantities of benzenesulfonyl chloride. After stirring mechanically until the odor of benzenesulfonyl chloride had disappeared (thirty to sixty minutes), the resulting precipitate was collected, washed with cold water and weighed. The crude product so obtained was recrystallized from the minimum quantity of 95% alcohol, when it separated in leaflets melting at 212° (corr.). The maximum yield (42%) of recrystallized product was obtained with 6.4 g. of sodium hydroxide; with 3.2 g. of alkali the yield was 17%; intermediate yields were obtained with intermediate quantities of alkali. With 8.6 g. the yield was only 30%. Decreasing the amount of benzenesulfonyl chloride to 4 cc. had only slight effect on the yield.

The pure product is no more readily soluble in cold aqueous alkali than in cold water; on boiling 0.250 g. with 200 cc. of *N* sodium hydroxide for twenty-four hours, 94.6% of the total amount of nitrogen was recovered as ammonia.

Benzenesulfonylguanidine hydrochloride was prepared by dissolving 0.5 g. of benzenesulfonylguanidine in 10 cc. of concentrated hydrochloric acid and evaporating the excess acid at room temperature in a current of air under reduced pressure. It melted at 160–163° (corr.).

Anal. Calcd. for $C_7H_{10}O_2N_3SCl$: Cl, 15.1. Found: Cl, 14.9.

The picrate separated in yellow needles, melting at 190–191° (corr.), on adding picric acid to a solution of benzenesulfonylguanidine in hot alcohol. On attempting to recrystallize from alcohol or ethyl acetate, dissociation took place with loss of picric acid.

The acetyl derivative was prepared by boiling benzenesulfonylguanidine for fifteen to thirty minutes with eight parts of acetic anhydride; m. p. 197–197.5° (corr.) from ethyl acetate.

Anal. Calcd. for $C_9H_{11}O_3N_3S$: S, 13.3. Found: S, 13.4.

The benzenesulfonyl derivatives of alkyl guanidines were prepared by the procedure which had been found to give the best yields with guanidine.

Benzenesulfonylmethylguanidine.—M. p. 180.5–181° (corr.).

Anal. Calcd. for $C_8H_{11}O_2N_3S$: C, 45.1; H, 5.20; N, 19.7; S, 15.0. Found: C, 45.2; H, 5.26; N, 19.2; S, 15.1.

Hydrochloride: M. p. 123–126° (corr.).

Anal. Calcd. for $C_8H_{12}O_2N_3SCl$: Cl, 14.2. Found: Cl, 14.0.

Benzenesulfonyl-*as*-dimethylguanidine.—M. p. 164.5–165.5° (corr.).

Anal. Calcd. for $C_9H_{13}O_2N_3S$: C, 47.6; H, 5.75; N, 18.4; S, 14.1. Found: C, 47.8; H, 5.65; N, 17.2; S, 14.1.

Benzenesulfonylpiperidoguanidine.—Three and one-half grams of a pure product, m. p. 168.5–169° (corr.), was obtained from 4 g. of piperidoguanidine sulfate.[4]

Anal. Calcd. for $C_{12}H_{17}O_2N_3S$: C, 53.9; H, 6.36; N, 15.7; S, 12.0. Found: C, 53.7; H, 6.28; N, 15.1; S, 11.7.

Monobenzenesulfonylarginine.—To a solution of 6 g. of arginine nitrate (0.025 m.) in 30 cc. of water were added 11 g. (0.08 m.) of potassium carbonate and 5 cc. of benzenesulfonyl chloride (0.039 m.). After stirring mechanically for a half hour at room temperature the clear solution was weakly acidified with 7 cc. of concentrated hydrochloric acid and evaporated to dryness under reduced pressure. The residue was extracted with ethyl alcohol; the alcoholic solution was again evaporated to dryness and taken up in the minimum quantity of alcohol. The glassy sirup left on evaporation was dissolved in 100 cc. of water and treated with 6 g. of picric acid in hot concentrated aqueous solution. The oily precipitate became crystalline on standing. On recrystallization from alcohol, 9.5 g. of yellow needles, melting at 161–162° (corr.), was obtained.

Anal. Calcd. for $C_{18}H_{21}O_{11}N_7S$: C, 39.8; H, 3.87; N, 18.0; S, 5.89; picric acid, 42.2. Found: C, 38.9; H, 4.02; N, 16.9; S, 5.60; picric acid, 41.9.

A 3% solution of the picrate in *N*/10 sodium hydroxide when treated by Van Slyke's method gave 4.2% of the amount of amino nitrogen theoretically obtainable from a corresponding quantity of arginine. This solution was mixed with an equal volume of concentrated hydrochloric acid, freed of precipitated picric acid by filtration, and boiled under reflux; 2-cc. portions removed at intervals were analyzed for amino nitrogen, the hydrochloric acid being neutralized by first adding 1.5 cc. of 25% sodium hydroxide and 0.5 cc. of acetic acid to the reaction mixture.

Hours boiling	0	1	3	8	16	24	44
Amino nitrogen, % of theoretical	4.2	17.0	24.1	43.8	68.6	79.7	106.0

Dibenzenesulfonylarginine.—To a solution of 4 g. of arginine monohydrochloride in 8 cc. of water was added 20 cc. of 25% sodium hydroxide solution; 6 cc. of benzenesulfochloride was added in two equal portions, the mixture being shaken vigorously after each addition. The temperature was not allowed to rise above 25°. After standing for half an hour, the mixture was freed of crystals (about 6 g., largely sodium benzenesulfonate), and the filtrate shaken with a further 3-cc. portion of benzenesulfochloride. After standing overnight, the mixture was rendered strongly acid with concentrated hydrochloric acid; the gummy precipitate was taken up by shaking with a mixture of butyl alcohol (75%) and ethyl acetate (25%). Undissolved salts were removed and the solution concentrated to a sirup. This was taken up in dioxane; the filtered solution was evaporated to a sirup and treated with excess of ethyl ether. The

sticky insoluble product was washed with ether, treated with 60 cc. of boiling water until free of steam-volatile and water-soluble impurities, and finally dried at 100°. On cooling, it formed a colorless resin, soluble in acetic acid, acetone, chloroform, ethyl acetate and ethyl alcohol, but insoluble in benzene, carbon tetrachloride, ethyl ether and water. A sample gradually dissolved in boiling sodium hydroxide solution, giving off the odor of butyl alcohol; it thus appeared to consist principally of the butyl ester of dibenzenesulfonylarginine.

Anal. Calcd. for $C_{22}H_{36}O_6N_4S_2$: C, 51.34; H, 6.79; N, 10.87; S, 12.42. Found: C, 50.4; H, 5.97; N, 10.43; S, 11.45.

Hydrolysis was effected by warming on the steam-bath a solution in ethyl alcohol to which small quantities of concentrated ammonia were added from time to time. After twelve hours no precipitation occurred on diluting with water; the solution was evaporated to dryness, and the residue taken up in boiling water, filtered hot and allowed to cool. The clear resin which separated was rinsed with water and dried at 100°; it appeared to consist of the ammonium salt.

Anal. Calcd. for $C_{18}H_{25}O_6N_5S_2$: N, 14.85; S, 13.59; acid equiv., 471. Found: N, 15.25; S, 11.9; acid equiv., 465.

The free acid was thrown out as an oil on adding a slight excess of mineral acid to a saturated solution of the ammonium salt in cold water. After rinsing with cold water and drying at 100° it solidified to a colorless resin, soluble in acetone, acetic acid, ethyl alcohol and hot water, but insoluble or sparingly soluble in benzene, carbon tetrachloride, chloroform, ethyl acetate and ethyl ether.

Anal. Calcd. for $C_{18}H_{22}O_6N_4S_2$: N, 12.34; S, 13.84. Found: N, 12.39; S, 13.07.

The authors wish to express their indebtedness to Mr. William Saschek for carrying out the microanalyses recorded in this paper.

Summary

The introduction of the benzenesulfonyl group into guanidine and its derivatives takes place only in the presence of strong alkalies, and not with alkali carbonates. Similarly, with arginine, the benzenesulfonyl group attaches itself only to the α-nitrogen atom in the presence of carbonate, but when alkali hydroxide is present in excess, the guanidine group is acylated as well.

Benzenesulfonyl guanidine is a weak base, and exhibits no tendency to form a sodium derivative analogous to that formed by benzenesulfonamide. It yields an acetyl derivative on treatment with acetic anhydride.

NEW YORK CITY

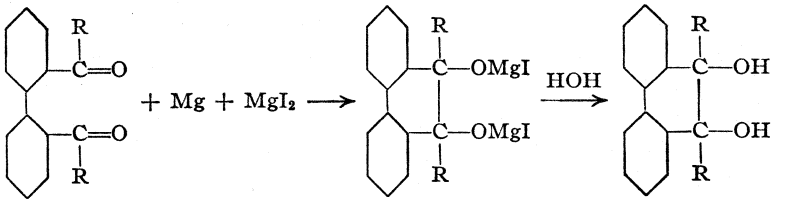
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REARRANGEMENT OF 9,10-DIARYLDIHYDROPHENANTHRENEDIOLS

BY W. E. BACHMANN

RECEIVED DECEMBER 14, 1931 PUBLISHED MAY 7, 1932

In continuing the study of the pinacol–pinacolin rearrangement,[1] we have investigated the rearrangement of a number of 9,10-diaryldihydrophenanthrenediols. These glycols correspond to pinacols and it appeared that they would be formed by the reduction of 2,2′-diacylbiphenyls by a mixture of magnesium and magnesium iodide in the same manner that ketones are reduced to pinacols.[2]



It was found that 2,2′-dibenzoylbiphenyl (R = C_6H_5) reacts with the binary mixture and is reduced to a mixture of stereoisomeric 9,10-diphenyldihydrophenanthrenediols. The product formed in the largest proportion is a pinacol which melts at 179–180°; a small amount of a pinacol melting at 202° is produced. Our products were found to be identical with the two stereoisomeric forms of diphenyldihydrophenanthrenediol that had been obtained by Werner and Grob[3] and by Acree[4] by other methods. These investigators prepared the low-melting pinacol by the action of phenylmagnesium bromide on phenanthrenequinone; the high-melting isomer was obtained by the reduction of dibenzoylbiphenyl by zinc and potassium hydroxide. On repeating the latter reaction we actually obtained a mixture of the two isomers and not a single compound.

Werner and Grob reported that the two isomeric diphenyldihydrophenanthrenediols when treated with a mixture of sulfuric acid and hydrochloric acid at 200° gave the same pinacolin, 10,10-diphenylphenanthrone (9). We have repeated the rearrangement reaction using acetyl chloride at a lower temperature and also acetic acid containing a small amount of iodine[2] in order to be certain that the product was not the result of a secondary action[5] but was the initial product of rearrangement.

[1] Bachmann and Moser, THIS JOURNAL, **54**, 1124 (1932).

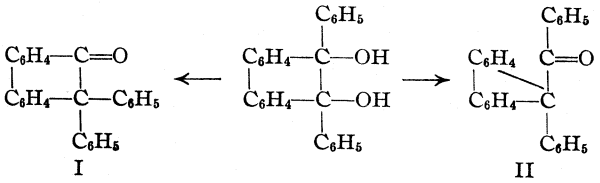
[2] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

[3] Werner and Grob, *Ber.*, **37**, 2887 (1904).

[4] Acree, *Am. Chem. J.*, **33**, 186 (1905).

[5] "Annual Reports," 1930, Vol. 27, p. 120; also Bergmann and Schuchardt, *Ann.*, **487**, 285 (1931).

Under these conditions each pinacol gave diphenylphenanthrone, showing that of the two possible rearrangements, I and II, only the mechanism I, involving the migration of the phenyl group, takes place.



I II

Since in symmetrical mixed pinacols the relative migration aptitudes of the *p*-tolyl and the anisyl groups were found to be greater than that of the phenyl group, it was predicted[1] that in the rearrangement of di-*p*-tolyldihydrophenanthrenediol and of dianisyldihydrophenanthrenediol the *p*-tolyl group and the anisyl group, respectively, would migrate practically exclusively. These new pinacols were synthesized and subjected to rearrangement. It is found that the predictions are confirmed. Rearrangement of di-*p*-tolyldihydrophenanthrenediol gives 10,10-di-*p*-tolylphenanthrone(9); dianisyldihydrophenanthrenediol gives 10,10-dianisylphenanthrone(9).

It was possible to prepare two stereoisomeric di-*p*-tolyldihydrophenanthrenediols and two stereoisomeric dianisyldihydrophenanthrenediols. A high-melting compound was obtained by reduction of the corresponding 2,2′-diacylbiphenyl by magnesium and magnesium iodide or by zinc and potassium hydroxide; a low-melting isomer resulted from the action of a Grignard reagent on phenanthrenequinone. The two stereoisomeric di-*p*-tolyldihydrophenanthrenediols were rearranged to the same pinacolin; in like manner the pair of dianisyldihydrophenanthrenediols gave the same compound on rearrangement. All of the pinacols are oxidized by chromic acid to the corresponding 2,2′-diacylbiphenyls.

The investigation of the rearrangement of substituted dihydrophenanthrenediols is being continued.

Experimental

Reduction of 2,2′-Dibenzoylbiphenyl by Mg + MgI_2.—Two grams of 2,2′-dibenzoylbiphenyl was added to a mixture of magnesium and magnesium iodide prepared from 2 g. of iodine and 1 g. of magnesium powder in 15 cc. of ether and 30 cc. of benzene; an insoluble oily complex of ketone and magnesium iodide precipitated. The mixture was refluxed until the oily complex had disappeared. The pinacol which was obtained on hydrolysis of the filtered solution was recrystallized from *n*-propyl alcohol. In this way there was obtained 1.1 g. of needle-like crystals of 9,10-diphenyldihydrophenanthrenediol melting at 202°; from the alcoholic filtrate 0.65 g. of the low-melting pinacol was isolated. When this latter product was recrystallized from acetic acid, it was obtained in the form of prisms melting at 179–180°. These prisms were found to be identical with the pinacol which was prepared by the action of phenylmagnesium bromide on phenanthrenequinone according to the directions of Acree.[4] Acree ob-

tained 25 g. of product from 20 g. of phenanthrenequinone. Recently, Schlenk and Bergmann[6] reported that they obtained only one-half of this yield. We obtained, in agreement with Acree, a yield of 26 g. of recrystallized pinacol from 20 g. of phenanthrenequinone.

When dibenzoylbiphenyl was treated with zinc and potassium hydroxide according to the directions of Werner and Grob, there was obtained a 76% yield of the high-melting pinacol and a 13% yield of the low-melting compound. Reduction of dibenzoylbiphenyl by zinc and acetic acid at room temperature gave the high-melting pinacol as the principal product; when the reaction was carried out in a warm solution the product was not pinacol but the pinacolin, diphenylphenanthrone.

Rearrangement of 9,10-Diphenyldihydrophenanthrenediol.—The product obtained by heating 1 g. of pinacol of m. p. 179–180° with a mixture of 10 cc. of acetyl chloride, 5 cc. of acetic acid and 20 cc. of benzene was practically pure 10,10-diphenylphenanthrone-(9). The same compound was obtained by rearrangement under the same conditions of the pinacol melting at 202°; from 0.5 g. of pinacol there was obtained 0.44 g. (92%) of pure diphenylphenanthrone.

2,2′-Di-*p*-toluylbiphenyl, $CH_3C_6H_4COC_6H_4C_6H_4COC_6H_4CH_3$.—This compound was prepared from 2-bromo-4′-methylbenzophenone by the Ullmann reaction. The substituted benzophenone was obtained by the action of the Grignard reagent from 17 g. of *p*-bromotoluene in 35 cc. of ether on 12 g. of *o*-bromocyanobenzene in 35 cc. of benzene. After twelve hours of refluxing, the reaction mixture was treated with water and the ketone-imine was hydrolyzed in the usual manner. The ketone was recrystallized from alcohol; yield, 15 g. (83%). Heidenreich[7] obtained this ketone from *o*-bromobenzoyl chloride and toluene. Our method of synthesis proves that it was the *p*-methyl derivative that was formed in the Friedel and Crafts reaction carried out by him.

A mixture of 2 g. of 2-bromo-4′-methylbenzophenone and 5 g. of copper powder was heated with stirring at 200° for one-half hour. The mass was cooled and extracted with acetone. Evaporation of the acetone gave 2,2′-di-*p*-toluylbiphenyl. Recrystallization from acetic acid gave needle-like prisms melting at 137°; yield, 0.95 g. (68%).

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.1; H, 5.7. Found: C, 85.9; H, 5.6.

Reduction of 2,2′-Di-*p*-toluylbiphenyl. (a) By Mg + MgI_2.—Two grams of 2,2′-di-*p*-toluylbiphenyl was added to a mixture of magnesium and magnesium iodide prepared from 2 g. of iodine and 1 g. of magnesium powder in 15 cc. of ether and 30 cc. of benzene. The mixture was refluxed until the insoluble oily complex of ketone and magnesium iodide had disappeared. The pinacol which was obtained by hydrolysis of the filtered solution was recrystallized from a mixture of benzene and alcohol. The product (1.8 g.) appeared to be a mixture of pinacols. When it was recrystallized from *n*-propyl alcohol, there was obtained 1.0 g. of di-*p*-tolyldihydrophenanthrenediol in the form of transparent prisms; m. p. 213°.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.7; H, 6.2. Found: C, 85.9; H, 6.2.

(b) By Zn + KOH.—One gram of 2,2′-di-*p*-toluylbiphenyl was dissolved in 40 cc. of 95% alcohol, several grams of zinc dust and 5 cc. of 40% potassium hydroxide solution were added and the resulting mixture was refluxed for eight hours. The solution was filtered and the filtrate was poured into water. The solid which precipitated was filtered off and recrystallized from *n*-propyl alcohol; m. p. 213°; yield, 0.6 g. (60%). This compound was identical with the product obtained by means of magnesium and magnesium iodide. From the filtrate 0.1 g. of pinacol melting at 136° was isolated.

[6] Schlenk and Bergmann, *Ann.*, **463**, 209 (1928).

[7] Heidenreich, *Ber.*, **27**, 1452 (1894).

9,10-Di-*p*-tolyldihydrophenanthrenediol (Low-melting Isomer).—To the Grignard reagent which had been prepared from 42 g. of *p*-bromotoluene in 80 cc. of ether was added 50 cc. of benzene and then 17 g. of phenanthrenequinone in portions. The mixture was refluxed for five hours, cooled and hydrolyzed. The crude ditolyldihydrophenanthrenediol which was obtained by evaporation of the ether–benzene solution was digested with cold alcohol in order to remove oily impurities and it was then recrystallized from a mixture of benzene and alcohol; m. p. 103°; yield, 18 g. (57%). When the product was recrystallized again from *n*-propyl alcohol the melting point remained unchanged. When, however, a small amount was recrystallized from ethyl alcohol, the melting point was changed to 136°. This represents a second modification of the compounds, for both behaved alike on oxidation and rearrangement. The low-melting form is very soluble in hot organic solvents; it crystallizes from acetic acid in needle-like prisms containing solvent of crystallization which melt at 84°. The 136° modification is not very soluble in cold or in hot alcohol but is readily soluble in hot acetone; it crystallizes from acetic acid without solvent.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.7; H, 6.2. Found: C, 85.3; H, 6.1.

Oxidation of 9,10-Di-*p*-tolyldihydrophenanthrenediol.—Eight grams of pinacol (m. p. 103°) was added to a solution of 1.6 g. of chromic anhydride in 4 cc. of water and 100 cc. of acetic acid. The mixture was warmed on a steam-bath for one-half hour and was then poured into water. The colorless solid which precipitated was filtered off and was recrystallized from acetic acid; yield of 2,2′-di-*p*-toluylbiphenyl, 6 g. (75%); m. p. 137°. The product was identical with 2,2′-di-*p*-toluylbiphenyl which was synthesized from 2-bromo-4′-methylbenzophenone by the Ullmann reaction.

In another run, oxidation of 1 g. of pinacol gave needles melting at 125.5–126.0°. This product proved to be a second form of di-*p*-toluylbiphenyl. This low-melting form can be converted to the modification melting at 137° by inoculation of an acetic acid solution of the low-melting form or of the melted compound with a crystal of the high-melting form.

Oxidation of 1 g. of pinacol of m. p. 136° gave 0.80 g. (80%) of 2,2′-di-*p*-toluylbiphenyl. In like manner oxidation of the pinacol of m. p. 213° gave an 80% yield of the diketone.

Rearrangement of 9,10-Di-*p*-tolyldihydrophenanthrenediol.—One-half gram of pinacol (m. p. 213°) was heated for five minutes with 3 cc. of acetic acid to which a crystal of iodine[2] had been added. Two cc. of alcohol saturated with sulfur dioxide was added in order to remove the iodine. On cooling, 0.41 g. of 10,10-di-*p*-tolylphenanthrone (9) melting at 159° crystallized out. From the filtrate an additional 0.04 g. of the same product was isolated, making a total yield of 95% of that theoretically possible. Bergmann and Schuchardt[8] report 158° for the melting point of di-*p*-tolylphenanthrone which they obtained by rearrangement of di-*p*-tolylbiphenylene ethylene glycol.

One-half gram of the pinacol of m. p. 103° was heated with acetic acid and iodine in the same manner; again the product was ditolylphenanthrone. Rearrangement by means of acetyl chloride gave the same product. Finally, the same compound resulted on rearrangement of the second modification (m. p. 136°) of this stereoisomeric pinacol.

2,2′-Dianisoylbiphenyl, $CH_3OC_6H_4COC_6H_4C_6H_4COC_6H_4OCH_3$.—The ketone, 2-bromo-4′-methoxybenzophenone,[7] was prepared by the action of anisylmagnesium bromide from 19 g. of *p*-bromoanisole on 12 g. of *o*-bromocyanobenzene; yield, 13 g. (69%). A mixture of 4.4 g. of this ketone and 10 g. of copper powder was heated at 200° for thirty minutes. Extraction of the cooled mass with acetone gave 2,2′-di-

[8] Bergmann and Schuchardt, *Ann.*, **487**, 225 (1931).

anisoylbiphenyl. The compound was recrystallized from acetic acid and was obtained in the form of needle-like prisms; yield, 1.6 g. (50%). The compound melted at 147°, then solidified and melted at 152–153°. The low-melting modification can be changed to the high-melting form by inoculation of a solution of the former with a crystal of the latter.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.6; H, 5.2. Found: C, 80.0; H, 5.4.

Reduction of 2,2′-Dianisoylbiphenyl.—Reduction of 1 g. of 2,2-dianisoylbiphenyl by a mixture of magnesium and magnesium iodide gave 0.62 g. of 9,10-dianisyldihydrophenanthrenediol. After two recrystallizations from *n*-propyl alcohol it was obtained in the form of prisms (0.43 g.); m. p. 188–190°. The pinacol is not very soluble in cold or in hot alcohol; it is somewhat more soluble in hot propyl alcohol.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.2; H, 5.7. Found: C, 79.3; H, 5.7.

By refluxing a mixture of 2.5 g. of 2,2′-dianisoylbiphenyl, 10 g. of zinc dust, 100 cc. of alcohol and 10 cc. of 40% potassium hydroxide for six hours, there was obtained 9,10-dianisyldihydrophenanthrenediol. From hot *n*-propyl alcohol there crystallized 1.3 g. of pinacol of m. p. 188–190°; from the filtrate a 10% yield of the stereoisomer melting at 154–155° was isolated.

Oxidation of the dianisyldihydrophenanthrenediol (m. p. 188–190°) by a solution of chromic anhydride in acetic acid gave an 80% yield of 2,2′-dianisoylbiphenyl; m. p. 152–153°.

9,10-Dianisyldihydrophenanthrenediol (Low-melting Isomer).—Seventeen grams of phenanthrenequinone was added in portions to the Grignard reagent which had been prepared from 46 g. of *p*-bromoanisole in 80 cc. of ether and 50 cc. of benzene. After being refluxed for six hours, the mixture was hydrolyzed. A viscous oil was obtained which partly crystallized after three weeks. The mass was digested with a cold mixture of benzene and alcohol; this dissolved the oil but not the crystals. By recrystallization from *n*-propyl alcohol the dianisyldihydrophenanthrenediol was obtained as heavy diamond-shaped plates; m. p. 154–155°; yield, 8 g.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.2: H, 5.7. Found: C, 78.9; H, 5.7.

Oxidation of 3.0 g. of this pinacol by a solution of 0.6 g. of chromic anhydride in 36 cc. of acetic acid and 2 cc. of water at 100° gave 2.52 g. (83%) of 2,2′-dianisoylbiphenyl.

Rearrangement of 9,10-Dianisyldihydrophenanthrenediol.—By heating 0.5 g. of dianisyldihydrophenanthrenediol (m. p. 154–155°) with 3 cc. of acetic acid containing a small amount of iodine, there was obtained 0.46 g. (95%) of 10,10-dianisylphenanthrone(9) melting at 151–152°. This product was found to be identical with dianisylphenanthrone which was synthesized in a yield of 80% by the action of dimethyl sulfate on bis-(*p*-hydroxyphenyl)-phenanthrone.[9]

The dianisyldihydrophenanthrenediol of m. p. 188–190° gave a quantitative yield of dianisylphenanthrone when it was treated with acetic acid and iodine.

Summary

The binary system Mg + MgI_2 reduces 2,2′-dibenzoylbiphenyl to a mixture of stereoisomeric diphenyldihydrophenanthrenediols. 2,2′-Di-*p*-toluylbiphenyl and 2,2′-dianisoylbiphenyl are reduced in the same manner to the corresponding substituted diaryldihydrophenanthrenediols.

The three pairs of stereoisomeric diaryldihydrophenanthrenediols readily undergo the pinacol–pinacolin rearrangement; in these rearrangements

[9] Goldschmidt, Vogel and Bredig, *Ann.*, **445**, 123 (1925).

migration of the phenyl, *p*-tolyl and anisyl groups occurs practically exclusively.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE INTERACTION OF AMIDES WITH ANILINE

BY CHARLES D. HURD, MALCOLM F. DULL AND K. E. MARTIN

RECEIVED DECEMBER 14, 1931 PUBLISHED MAY 7, 1932

Very little information is to be found in the literature regarding the interaction of amides with aniline. To study this question, two methods were chosen: (1) to leave the amides in contact with aniline for varying periods at several temperatures, and (2) to conduct the amide vapors through a hot tube, discharging them into cold aniline.

Except for a catalytic transformation of acetamide into methylamine (or HCN + H_2) and carbon monoxide using nickel[1] at 400°, the only recorded course of pyrolysis of acetamide is the one into acetonitrile[2] and water. In our high temperature experiments there was the possibility of deammonation into ketene. With acetamide the equation would be $CH_3CONH_2 \longrightarrow CH_2CO + NH_3$. If so, the acetanilide might originate either from acetamide or ketene.

Actually, aniline was found to be quite non-reactive at 100° with such amides as acetamide, propionamide or isobutyramide. In fact, a mixture of the amide and aniline could be distilled (to 240°) without giving rise to anilide in the residue. Continued refluxing, however, was found to generate small yields of anilide, the best yields coming from propionamide. It was found that isobutyramide was exceedingly sluggish.

When the amides were passed through a tube which was maintained at 500–700°, some pyrolysis undoubtedly occurred because of nitrile formation. By passing the hot, effluent gases directly into cold aniline, fairly good yields of propionanilide or acetanilide, but no isobutyranilide, were obtained. The data for a few representative runs out of seventy-five which were performed are collected in Table I. The percentage yield of anilide is based on the amide which was not recovered. Examination of the data shows the best yields of acetanilide and propionanilide at tube temperatures of about 500° and contact times of but a few seconds. As high as 45–49% yields of propionanilide resulted, as compared with a 28% yield of acetanilide and no yield of isobutyranilide. Somewhat higher yields of acetanilide were obtained on a few occasions, but the selected runs seem more characteristic.

[1] Mailhe, *Mat. grasses*, **15**, 6488, 6531 (1923); *Bull. soc. chim.*, **37**, 1394 (1925).

[2] Boehner and Andrews, THIS JOURNAL, **38**, 2503 (1916); Boehner and Ward, *ibid.*, p. 2505.

Whether or not ketene and methyl ketene were pyrolytic products cannot be answered. If they were, they never persisted in the gases when a condenser (to remove amide, etc.) was inserted between the hot tube and the cold aniline. To establish whether or not an amide as such could react with aniline, benzamide was passed through the hot tube and thence into cold aniline. In this case there exists no possibility of deammonation into a ketene, yet a 33% yield of benzanilide was obtained. While this does not eliminate the possibility of ketenes as intermediates in the case of acetamide and propionamide, certainly they are not essential intermediates for anilide formation.

Experimental Part

Liquid Phase Experiments.—When 15 cc. of aniline was left for four hours with 5 g. of either acetamide, propionamide or isobutyramide[3] and then distilled at 20 mm. until the aniline and amide were removed, no residue of the anilide remained. Heating

TABLE I

DATA FOR HOT TUBE REACTIONS OF AMIDES

Temp., ±5°C.	Amide, g. Taken	Recov.	Inner diam. tube, cm.	Duration, min.	Hot contact time, sec.	Nitrile, g.	%	Water, g.	Anilide, g.	%
					Acetamide					
505	50	33	2.2	20	3.4	6.3	53.5	..	10.6	27.2
510	50	24.5	1.6	17	2.5	9.5	51.6	4.0	17	28.1
505	50	12.1	1.6	62	8.8	15.7	59.6	9.3	25	28.8
550	50	9.8	1.6	33	4.5	20	71.6	11.6	18	19.5
600	50	14.5	1.6	16	1.8	20.5	83.3	9.3	8.5	10.4
650	50	3.0	1.6	23	3.2	27.6	84.5	14.8	2.8	2.6
710	50	0.0	1.6	16	1.8	24.2	69.8	13.1	7.5	6.6
710	50	0.0	1.6	21	2.4	24.5	70.6	13.3	1.5	1.3
					Propionamide					
505	40	17.5	1.1	12	0.9	2.5	14.8	1.0	22.5	49.1
500	75	35.5	1.6	20	2.5	5.5	18.5	2.5	36.5	45.3
500	40	16.0	1.6	8	1.8	3.0	16.6	1.0	24.0	49.0
530	50	32.5	2.2	25	5.1	7.0	53.1	4.2	10.0	28.2
545	40	18.0	1.1	10	0.7	5.5	33.2	2.0	20.5	45.6
560	50	22	2.2	15	2.9	12.0	57.0	5.1	14.0	24.5
645	50	5	2.2	90	16.0	12.5	36.9	11.0	2.5	2.7
					Isobutyramide					
510	50	47.8	1.6	20	4.2	Trace		Trace	Nil	0.0
650	50	12.5	1.6	20	3.6	20.0	67.5	8.0	Trace	0.0
					Benzamide					
500	50	6.2	1.6	16	5.1	22.1	59.2	..	23.5	33

[3] By stirring a mixture of ethyl isobutyrate (250 g.) and concd. ammonium hydroxide (1 liter), an 80% yield of isobutyramide resulted in fifty days, whereas the yield was negligible in five days.

the mixtures for an hour at 100° prior to distillation gave no acetanilide or isobutyranilide but yielded a minute quantity of propionanilide. Reaction was produced by refluxing. When equal weights (20 g. each) of aniline and the three amides (three separate experiments) were refluxed for forty minutes, ammonia was evolved. Distillation at atmospheric pressure to 240° revealed a 13.7% yield of acetanilide, a 17% yield of propionanilide and a 5% yield of isobutyranilide: $RCONH_2 + C_6H_5NH_2 \longrightarrow RCONHC_6H_5 + NH_3$.

Reaction of Cold Aniline with Hot Amide Vapors.—Each amide was distilled in turn into a quartz or Pyrex combustion tube, packed with porcelain chips, which was heated by an electric furnace. A slow stream of nitrogen was blown through the system to maintain a uniform flow of the vapors. Experiments were performed at temperatures varying from 400 to 800°, the temperature being measured by a thermocouple placed inside of the tube. The thermocouple wires were encased in a sealed-off piece of Pyrex tubing. The vapors passed from the hot tube into a flask containing an excess of ice-cold aniline. Any carbon which formed was burned from the tube at the end of each run.

Distillation methods were used in working up the contents of the aniline solution. The nitrile and water were taken off below 105°. Aniline was then collected to 200° and the original amide between 200–240°. For the most part, the residue was the anilide, which was recrystallized from water.

The details of seventeen out of seventy-five experiments have been collected in Table I. Less than a liter of gases, collected over water, was formed in the 500° experiments. At 800°, the volume was 5 to 6 liters. Carbon monoxide was present, together with lesser amounts of carbon dioxide and methane.

Summary

Amides do not react with aniline at room temperature or at 100° but refluxing for an extended period gives rise to small yields of anilides. Amide vapors issuing from hot tubes were found to react with cold aniline to give fair yields of anilides. These results were obtained with acetamide, propionamide and benzamide, but isobutyramide gave almost negligible yields in all cases. The possibility of ketene formation from amides was discussed.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPYRIDYLS. PREPARATION AND RESOLUTION OF 2,4,2′,4′-TETRACARBOXY-6,6′-DIPHENYL-3,3′-DIPYRIDYL. XX[1,2]

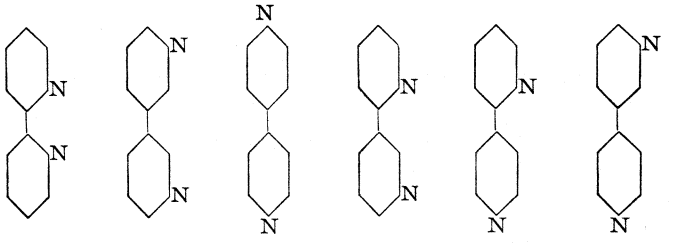
BY E. H. WOODRUFF AND ROGER ADAMS

RECEIVED DECEMBER 19, 1931 PUBLISHED MAY 7, 1932

The extension of the study of optical isomerism in certain substituted diphenyls to other binuclear ring systems has already been accomplished in certain cases, notably the N-phenylpyrroles, the N,N′-dipyrryls, and the phenylquinones. However, attempts to obtain optically active compounds with a phenyl and a heterocyclic ring linked through a —C—C— linkage have thus far met with failure.

Steele and Adams[3] and Lions[4] have reported several unsuccessful attempts to resolve a —C—C— linked phenylpyridine. In spite of this fact it still seemed probable that with correctly selected groups in the *o*-positions, especially if all four positions are substituted, compounds might be found which could be resolved.

In this communication the study of a substituted dipyridyl is reported. There are six types of dipyridyls containing —C—C— linkage. The unsubstituted compounds are all known.[5]



If such molecules are analogous to diphenyl compounds, it might be anticipated that resolvable compounds of Type I and possibly of Types IV and V might not exist unless, perhaps, the nitrogen atoms were converted to quaternary ammonium groups.

A compound of the general type (II) has been prepared and resolved into optically active isomers. It is 2,4,2′,4′-tetracarboxy-6,6′-diphenyl-

[1] This communication is an abstract of a thesis submitted by E. H. Woodruff in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

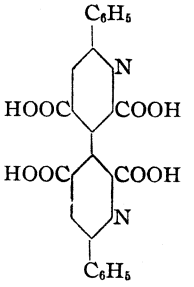
[2] The previous papers in this field are: Bock and Adams, THIS JOURNAL, **53**, 3519 (1931); Hill and Adams, *ibid.*, **53**, 3453 (1931).

[3] Steele and Adams, *ibid.*, **52**, 4528 (1930).

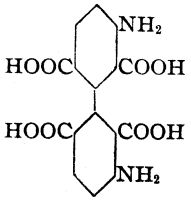
[4] Lions, *ibid.*, **53**, 1176 (1931).

[5] C. R. Smith, THIS JOURNAL, **46**, 414 (1924).

3,3′-dipyridyl (VII). The active forms have rotations, $[\alpha]_D$ +6.1°, $[\alpha]_D$ −5.9°, and readily racemize upon warming in alcohol solution. It would appear, then, that the resistance to free rotation between the rings is very slight. It is probable that the interfering effect of two of the carboxyl groups is partially diminished due either to the smaller size of the ions found because of the presence of the basic nitrogen, or to the electrical characteristics of the ions or to the distortion of the forces on account of the internal neutralization of the carboxyl and the nitrogens. It is quite probable, moreover, that the character of a pyridine ring as regards conditions necessary for resolution of phenylpyridines and dipyridyls is different from that of benzene. Such a dipyridyl as has been described in this communication is quite analogous to a diphenyl of the formula 2,6,2′,6′-tetracarboxy-3,3′-diaminodiphenyl (VIII) which has not yet been prepared. By past



VII



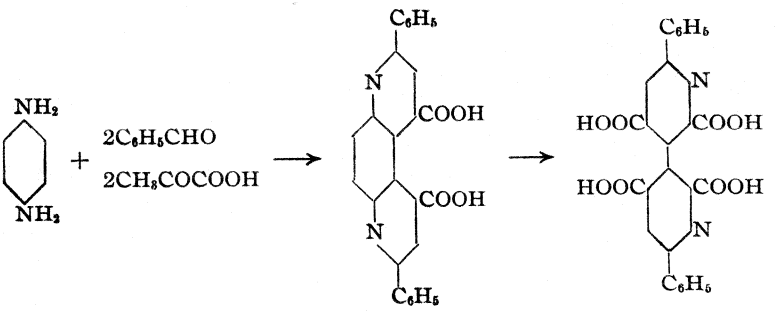
VIII

experience it would be expected that any ortho-tetracarboxydiphenyl with the two rings asymmetrically substituted but without other complicating factors should be relatively stable to racemization. However, in the diamino derivative the interfering effect of the two carboxyls adjacent to the two amines might be lessened to such an extent that the active compound would racemize readily.

The 2,4,2′,4′-tetracarboxy-6,6′-diphenyl-3,3′-dipyridyl was synthesized by the following reactions. *p*-Phenylenediamine was condensed with benzaldehyde and pyruvic acid to 1,10-dicarboxy-3,8-diphenyl-4,7-phenanthroline. Although the exact structure of this compound was not determined, the conclusion that both nitrogen rings closed toward each other in the position indicated is supported by the results of previous investigators,[6] who have proved that the unsubstituted phenanthroline made from *p*-phenylenediamine by the Skraup synthesis has the pyridine rings closed on the same side of the benzene ring. Moreover, the other isomeric phenanthroline could hardly be expected to oxidize to a tetrabasic acid.

Upon oxidation of the phenanthroline with potassium permanganate, the tetracarboxydipyridyl was obtained and resolved through the di-

[6] Döbner and Ferber, *Ann.*, **281**, 16 (1894).



brucine salt. The chief difficulty involved was the isolation of the product due to the fact that the phenanthroline and tetracarboxydipyridyl are both acidic in character and rather similar in solubility.

Experimental

1,10-Dicarboxy-3,8-diphenyl-4,7-phenanthroline.—To 55 g. of *p*-phenylenediamine dissolved in 1 liter of boiling 95% alcohol in a 2-liter beaker was added 106 g. of benzaldehyde. The solution was then allowed to cool slightly until the Schiff base started to separate in the form of green-golden plates. The solution was then reheated to boiling and 88 g. of freshly prepared pyruvic acid was added with stirring over a period of five minutes in 10-cc. amounts. The reaction mixture boils violently so that the addition of pyruvic acid should not be too rapid. The solution, now deep red in color, was evaporated on a hot-plate to a total volume of 300–400 cc., when it was poured into a hot solution consisting of 60 g. of potassium hydroxide in 1500 cc. of distilled water. The solution was further evaporated until the volume reached about 1000 cc. in order that all of the alcohol would be removed. Then 1 liter of water was added and the solution was allowed to cool and stand. The by-product separated as a tar which solidified when cool. The solution was then filtered through norite. (This solution can now be used without further purification for the oxidation subsequently described.)

The isolation of the substituted phenanthroline was accomplished by heating the solution to 80–90° and acidifying with dilute hydrochloric acid. The product separated immediately in a crystalline condition and was filtered. If the solution was acidified when cold, the phenanthroline precipitated in an amorphous condition and was filtered and dried only with difficulty. The yield was 90–110 g. (42–50%).

Purification was accomplished by redissolving in a liter of hot potassium hydroxide solution (containing 40 g. of solid potassium hydroxide), filtering and reprecipitating with hydrochloric acid while hot. After cooling and filtering, the product could be crystallized from alcohol as follows. The dried material was dissolved in 300 cc. of hot 95% alcohol and filtered. It was then cooled in ice and salt and a small amount of material separated. The major portion did not appear until cooled to the temperature of a carbon dioxide–ether mixture. The product from alcohol is a deep brick red after it is dried and finely divided; yield 42 g. It may also be recrystallized from water, from which it separates as a bright scarlet material. The melting point is 250.5–251.5°, with decomposition.

Anal. Calcd. for $C_{26}H_{16}O_4N_2$: C, 74.26; H, 3.84; N, 6.66. Found: C, 74.20; H, 4.13; N, 6.68.

The di-silver salt of this compound was also prepared. A small amount of the acid (0.5–1.0 g.) was dissolved in 25 cc. of water containing a few drops of concentrated aqueous ammonia. The solution was then boiled to expel the excess ammonia and fil-

tered into a hot aqueous solution of silver nitrate. The di-silver salt separated as a yellow flocculent precipitate which was filtered with suction, washed with hot water and then with hot acetone.

Anal. Calcd. for $C_{26}H_{14}O_4N_2Ag_2$: Ag, 34.04. Found: Ag, 33.60.

2,4,2',4'-Tetracarboxy-6,6'-diphenyl-3,3'-dipyridyl.[7]—A solution of 21 g. of 1,10-dicarboxy-5,8-diphenyl-4,7-phenanthroline in 6 g. of potassium hydroxide, dissolved in 1 liter of water, was placed in a 2-liter beaker. Cracked ice was added to cool the solution to 10–15°, at which point a solution of 30 g. of potassium permanganate in 400 cc. of hot water was added with rapid stirring. This caused the temperature of the solution to rise to 20–25°. If the oxidation was carried out below this temperatrre, the manganese oxides formed did not coagulate properly and made filtration difficult. The solution was allowed to stand for one hour, after which time it was heated on a steam cone to coagulate further the oxides of manganese. After standing, the oxides settled and about one-half of the liquid could be decanted before filtration.

The filtered solution was placed in a large porcelain evaporating dish and was acidified with concentrated nitric acid to Congo red paper. The solution was then evaporated to dryness on a steam cone and the crude acids were extracted from the salt with acetone. The acetone solution, after filtration, was evaporated to dryness and the last traces of solvent removed in a vacuum desiccator. The dry product was boiled with 300 cc. of ethyl acetate and the hot solution filtered into 900 cc. of petroleum ether (b. p. 65–110°).

The precipitate was filtered with suction and partially dried by allowing the air to pass through for about fifteen minutes. This solid was then redissolved in 100 cc. of boiling ethyl acetate and the procedure repeated. This was again done, using about 50 cc. of ethyl acetate. This series of precipitations serves to remove the phenanthroline, which is only slightly soluble in ethyl acetate.

The removal of the last traces of solvent can be accomplished by a final drying in an Abderhalden dryer over phosphorus pentoxide at a temperature of 100° (water). About 7.5 g. of product was obtained as a light yellow powder, which decomposes without melting at 181°.

Anal. (Micro). Calcd. for $C_{26}H_{16}O_8N_2$: C, 64.44; H, 3.33: N, 5.78. Found: C, 64.13, 64.24; H, 3.51, 3.41; N, 5.16.

Resolution of 2,2',4,4'-Tetracarboxy-6,6'-diphenyl-3,3'-dipyridyl.—Two methods of resolution were used. The first was more extensively studied but the second proved much the simpler of the two.

First Method.—A solution of 4.84 g. (0.01 mole) of the tetracarboxydipyridyl in 200 cc. of ethyl acetate and a solution of 7.88 g. (0.02 mole) of brucine in 200 cc. of ethyl acetate were mixed together in a 2-liter beaker. Sufficient ethyl acetate was then added to dissolve almost completely the brucine salt. The hot solution was filtered, cooled and the precipitated salt filtered out by means of a Gooch crucible. About 0.5 g. was usually obtained.

Rotation. 0.2205 g. made up to 50 cc. with chloroform at 20° gave α_D $-0.02 \pm 0.01°$; $l = 1$; $[\alpha]_D^{25}$ $-4.9°$.

This precipitate was extracted several times with 100-cc. portions of hot ethyl acetate, but neither the residue nor the salt which separated on cooling showed any change in rotation.

The filtrate from the 0.5 g. of salt from the original solution was then concentrated and various fractions as they precipitated were filtered. This was continued until a volume of 50 cc. was reached when no more salt could be obtained in a solid condition

[7] Skraup and Vortmann, *Monatsh.*, **4**, 583 (1883).

upon cooling the solution. These intermediate fractions were worked up for less soluble and more soluble salt by the process just discussed.

Upon evaporating the 50 cc. to dryness and removing the last traces of solvent by suction, the more soluble salt was obtained in a dry powdery form. Generally less than a gram was obtained.

Rotation. 0.1136 g. made up to 20 cc. with chloroform at 20° gave α_D −0.20 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ −35.8°.

Second Method.—To a solution of 9.682 g. (0.02 mole) of the acid in 200 cc. of ethyl acetate was added 7.88 g. (0.02 mole) of brucine in 100 cc. of ethyl acetate. A precipitate (8.7 g.) was obtained which decomposed without melting at 202–207°. It was purified by boiling with ethyl acetate to dissolve any more soluble salt which had adhered.

Rotation. 0.1400 g. made up to 50 cc. with chloroform at 20° gave α_D −0.01 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ −3.5°.

Upon the addition of another 7.88 g. (0.02 mole) of brucine in 100 cc. of ethyl acetate, 1.9 g. more of precipitate was obtained which apparently was a less soluble form.

Rotation. 0.1623 g. made up to 50 cc. with chloroform at 20° gave α_D −0.046 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ −5.6°.

The solution was then evaporated to 50 cc., whereupon 14 g. of salt had precipitated.

Rotation. 0.1916 g. made up to 20 cc. with chloroform at 20° gave α_D −0.19 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ −19.8°.

The last 50 cc. was evaporated to dryness and 3 g. of more soluble salt was obtained. It turns brown at 155–160° and melts with decomposition at 180–184°.

Rotation. 0.1500 g. made up to 20 cc. with chloroform at 20° gave α_D −0.26 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ −34.7°.

By extracting the 14 g. of intermediate fraction with 50-cc. portions of the ethyl acetate, 1.5 g. of the more soluble salt was readily obtained having $[\alpha]_D^{25}$ −35°.

Anal. Calcd. for $C_{72}H_{68}N_6O_{16}$: N, 6.69. Found: for less soluble salt, N, 6.61; for more soluble salt, N, 6.66.

d and *l*-2,2′-4,4′-tetracarboxy-6,6′-diphenyl-3,3′-dipyridyl.—Three grams of the salt $[\alpha]_D^{25}$ −5.0° was triturated in a small porcelain mortar with ice-cold, 5% hydrochloric acid, filtered and washed with distilled water. After partially drying, the procedure was repeated. The acid was then taken up in ice-cold, very dilute sodium hydroxide and shaken three times with 100-cc. portions of chloroform. The solution was filtered into cold dilute hydrochloric acid. (The procedure occupied about twenty minutes up to this point.) The free acid separated and was filtered and washed with distilled water and dried over phosphorus pentoxide *in vacuo* at room temperature. About 0.8 g. of the acid (entirely free from brucine) was recovered from the 3 g. of salt.

Rotation. 0.0896 g. made up to 20 cc. with acetone at 20° gave α_D +0.035 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ +7.8°. 0.1628 g. made up to 20 cc. with 95% alcohol at 20° gave α_D +0.05 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ +6.1°.

The same procedure was followed with the more soluble salt. The yield of free acid was less from this fraction.

Rotation. 0.0677 g. made up to 20 cc. with 95% alcohol at 20° gave α_D −0.04 ± 0.01°; $l = 2$; $[\alpha]_D^{25}$ −5.9°.

Anal. Calcd. for $C_{26}H_{16}N_2O_8$: N, 5.78. Found: for +6.1° acid, N. 5.16; for −5.9° acid, N, 5.08.

Racemization Tests.—0.3705 g. made up to 50 cc. with 95% alcohol at 20° gave α_D +0.04 ± 0.01°; $l = 1$; $[\alpha]_D^{25}$ +5.4°. The solution was allowed to stand at room temperature for twenty hours (T = 33–35°). α_D +0.02 ± 0.01°; $[\alpha]_D^{25}$ +2.7°.

The solution was then boiled for fifteen minutes, after which the rotation was 0.

Due to the deep color of the sodium salt, no rotation could be observed on account of the extreme dilution which was necessary before light would pass through the tube.

Summary

1. 2,4,2′,4′-Tetracarboxy-6,6′-diphenyl-3,3′-dipyridyl has been prepared by the oxidation of 1,10-dicarboxy-3,8-diphenyl-4,7-phenanthroline. This in turn was prepared by the condensation of *p*-phenylenediamine with benzaldehyde and pyruvic acid.

2. The dipyridyl was resolved through the brucine salt. The active acid was readily racemized by warming for a short time in ethyl alcohol.

URBANA, ILLINOIS

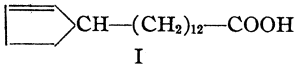
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION OF VARIOUS OMEGA-CYCLOHEXYL ALKYL AMINES AND THEIR BACTERICIDAL ACTION TO MYCOBACTERIUM LEPRAE. XXII[1]

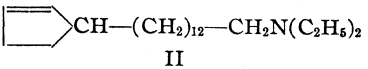
BY GERALD H. COLEMAN AND ROGER ADAMS

RECEIVED DECEMBER 21, 1931 PUBLISHED MAY 7, 1932

In one of the earlier papers[2] describing the preparation and bactericidal properties of various aliphatic acids, it was demonstrated in the case of chaulmoogric acid (I) that the carboxyl group could be replaced by a $-CH_2N(C_2H_5)_2$ group and the product (II) still had bactericidal properties.

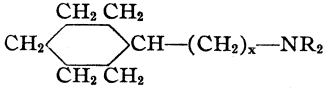


I



II

The present investigation involved the synthesis of a series of ω-cyclohexyl-alkyl tertiary amines of varying molecular weight and of the general formula (III).

III  R = C_2H_5, C_3H_7 or C_4H_9; x = 1 to 5

These compounds correspond essentially to the series of acids described in earlier papers.

The bacteriological study was made with the same strain of *Mycobacterium leprae* used with the acids. The amines were made into the hydrochloride salts and tested in the same manner as the sodium salts of the acids.[1b] The table (I) of results is given below.

The conclusions are very definite. The bactericidal value is dependent, in part at least, on molecular weight just as in the acids. It is obvious

[1] For the last three papers in this series see (a) Stanley, Coleman, Greer, Sacks and Adams, *J. Pharmacol.* (June, 1932); (b) Stanley and Adams, THIS JOURNAL, **54**, 1548 (1932); (c) Greer and Adams, *ibid.*, **52**, 2540 (1930).

[2] Sacks and Adams, *ibid.*, **48**, 2395 (1926).

TABLE I

CYCLOHEXYL SUBSTITUTED AMINES, $C_6H_{11}(CH_2)_xNR_2 \cdot HCl$

	Dilution of hydrochloride salts in thousands												
	5	10	20	22	27	35	50	70	80	100	125	155	200
$C_6H_{11}NH_2 \cdot HCl$	+	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}CH_2NH_2 \cdot HCl$	+	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}(CH_2)_2NH_2 \cdot HCl$	±	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}N(C_2H_5)_2 \cdot HCl$	+	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}CH_2N(C_2H_5)_2 \cdot HCl$	+	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}(CH_2)_3N(C_2H_5)_2 \cdot HCl$	−	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}(CH_2)_4N(C_2H_5)_2 \cdot HCl$	−	−	±	+	+	+	+	+	+	+	+	+	+
$C_6H_{11}(CH_2)_5N(C_2H_5)_2 \cdot HCl$	−	−	−	−	−	+	+	+	+	+	+	+	+
$C_6H_{11}(CH_2)_6N(C_2H_5)_2 \cdot HCl$	−	−	−	−	−	−	−	−	−	−	+	+	+
$C_6H_{11}(CH_2)_4N(C_3H_7)_2 \cdot HCl$	−	−	−	−	−	−	±	±	+	+	+	+	+
$C_6H_{11}(CH_2)_4N(C_4H_9)_2 \cdot HCl$	−	−	−	−	−	−	±	−	±	+	+	+	+
$C_6H_{11}(CH_2)_5N(C_3H_7)_2 \cdot HCl$	−	−	−	−	−	−	−	−	−	−	−	±	+

from the table that the molecules containing fifteen to eighteen carbon atoms show marked bactericidal action, but the action is insignificant or nil in the smaller molecules. The distribution of the carbon atoms in the cyclohexylalkyl residue or in the alkyl groups has, apparently, very little effect.

Presumably the proper combination of physical properties exists in these amine salts as in the salts of the acids. From these results it would appear that the carboxyl group and the amine group in bactericidal compounds of equal molecular weight may be interchangeable, though the bactericidal value of the amines is less than in the corresponding acids.

The amines were prepared by condensing the proper bromide with the secondary amines and the hydrochlorides were formed by precipitation with dry hydrogen chloride from a dry ether solution of the bases. The intermediate bromides were the same as those used in the synthesis of ω-cyclohexylalkyl aliphatic acids.[3]

Experimental

Cyclohexylamine was prepared according to the method of Hiers and Adams,[4] b. p. 132–133°; hydrochloride salt, after crystallization from chloroform and petroleum ether, m. p. 202°.

Cyclohexylmethylamine,[5] b. p. 159.5–160°; hydrochloride salt after crystallization from chloroform and petroleum ether, m. p. 252–253°.

β-Cyclohexylethylamine[5] was prepared from cyclohexylethyl bromide. A mixture of 10 g. of cyclohexylethyl bromide and 9.8 g. of potassium phthalimide was refluxed in a 100-cc., round-bottomed flask at 230–250° for seven hours. The mixture was cooled and extracted with 125 cc. of absolute alcohol. After evaporating the alcohol, the product was refluxed for one-half hour with 50 cc. of 10% potassium hydroxide solution and then for one-half hour after the addition of 10 cc. of concentrated hydrochloric acid.

[3] Hiers and Adams, THIS JOURNAL, **48**, 2385 (1926).

[4] Hiers and Adams, *Ber.*, **59**, 162 (1926).

[5] Wallach, *Ann.*, **353**, 297 (1907).

The solution was cooled, made alkaline, and ether extracted. The base was dried and distilled and converted to the hydrochloride; hydrochloride salt, m. p. 245–246°.

Cyclohexyldiethylamine was prepared by the method of Sabatier and Senderens:[6] b. p. 56–57° at 5 mm.; n_D^{25} 1.4560; d_{25}^{25} 0.8445; hydrochloride from benzene and petroleum ether, m. p. 152–153°.

General Method of Preparation of Amines and their Salts.—About 20 g. of bromide was mixed with three molecular equivalents of dialkyl amine and allowed to stand at room temperature. Crystals of hydrobromide separated. About 100 cc. of water was added and the solution, after acidification with hydrochloric acid, was ether extracted to remove unreacted bromide, then made alkaline and again ether extracted to remove the product. The base was dried with solid potassium hydroxide, then with metallic sodium and fractionated.

The hydrochlorides were prepared by dissolving the amines in dry ether, precipitating by passing in dry hydrogen chloride and recrystallizing the crude products from a suitable solvent. Excess of hydrogen chloride should be avoided; otherwise the hydrochlorides may separate as oils. These oils may be converted into crystalline products by evaporating the solvent, adding chloroform, re-evaporating, and recrystallizing with or without the addition of a second solvent such as petroleum ether.

TABLE II

ω-CYCLOHEXYLALKYL TERTIARY AMINES, $C_6H_{11}(CH_2)_xN(C_2H_5)_2$

X =	B. p., °C.	n_D^{25}	d_{25}^{25}	Time of standing in preparation, weeks
1	73–75 (3.5 mm.)	1.4551	0.8361	5
2	81–82 (3 mm.)	1.4582	.8421	4
3	95–98 (3 mm.)	1.4587	.8392	2
4	109–111 (3 mm.)	1.4613	.8414	2
5	124–126 (3 mm.)	1.4620	.8445	4

ω-Cyclohexylalkyl Tertiary Amine Hydrochlorides, $C_6H_{11}(CH_2)_xN(C_2H_5)_2\cdot HCl$

X =	M. p., °C.	Solvent for recrystallization	Calculated for	Chlorine, % Calcd.	Found
1	168–168.5	Benzene and ether	$C_{11}H_{23}N\cdot HCl$	17.28	17.30
2	155–156	$CHCl_3$ and CCl_4	$C_{12}H_{25}N\cdot HCl$	16.18	16.19
3	123–124	CCl_4 and pet. ether	$C_{13}H_{27}N\cdot HCl$	15.20	15.06
4	132–133	Abs. alc. and ether	$C_{14}H_{29}N\cdot HCl$	14.34	14.35
5	133–134	Abs. alc. and ether	$C_{15}H_{31}N\cdot HCl$	13.58	13.58
6	128–129	Abs. alc. and ether	$C_{16}H_{33}N\cdot HCl$	...	...

TABLE III

ω-CYCLOHEXYLALKYL TERTIARY AMINES, $C_6H_{11}(CH_2)_xNR_2$

X =	R =	B. p., °C.	n_D^{25}	d_{25}^{25}	Time of standing in preparation
4	n-C_3H_7	119–121 (2 mm.)	1.4598	0.8427	4 days
4	n-C_4H_9	135–138 (1.5 mm.)	1.4617	.8441	4 days
5	n-C_3H_7	143–144 (2.5 mm.)	1.4628	.8489	4 weeks

ω-Cyclohexylalkyl Tertiary Amine Hydrochlorides, $C_6H_{11}(CH_2)_xNR_2\cdot HCl$

X =	R =	M. p., °C.	Solvent for recrystallization	Calcd. for	Chlorine, % Calcd.	Found
4	n-C_3H_7	120–121	Abs. alc. and ether	$C_{16}H_{33}N\cdot HCl$	12.89	13.02
4	n-C_4H_9	91–91.5	Abs. alc. and ether	$C_{18}H_{37}N\cdot HCl$	11.70	11.76
5	n-C_3H_7	103–104	Abs. alc. and ether	$C_{17}H_{35}N\cdot HCl$	12.27	12.30

[6] Sabatier and Senderens, *Compt. rend.*, **138**, 1258 (1904).

Summary

It has been shown that ω-cyclohexylalkyl amines of the general formula $C_6H_{11}(CH_2)_xNR_2$ are bactericidal to *B. leprae* providing the molecules have the proper molecular weight. The compounds should contain fifteen to eighteen carbon atoms just as found necessary in the various acids already tested, distribution of the carbon atoms having very little effect.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA AND SYRACUSE UNIVERSITY]

THE IDENTIFICATION OF MERCAPTANS WITH 2,4-DINITROCHLOROBENZENE

BY R. W. BOST, J. O. TURNER AND R. D. NORTON

RECEIVED DECEMBER 21, 1931 PUBLISHED MAY 7, 1932

Due to the increasing interest shown in mercaptans and due to the paucity of good reagents whereby they may be identified, it seemed desirable to study methods for their identification. Numerous mercaptides[1,2,3] have been prepared. Purification of these is not always easy and certain of the mercaptides are frequently unstable.[4] Wertheim[1] has proposed 3,5-dinitrobenzoyl chloride and also 3-nitrophthalic anhydride as reagents for mercaptan identification. The use of these reagents is restricted, due to the close proximity of the melting points of certain of their derivatives. Reid[5] and his co-workers have suggested the use of sodium anthraquinone α-sulfonate and also sodium anthraquinone 1,5- and 1,8- disulfonates, although the sulfonic group could not be replaced with phenyl mercaptan. The time required for these reactions to go to completion varies from a few minutes to several hours, while in certain cases several products are obtained.

In this paper the authors propose 2,4-dinitrochlorobenzene as a new reagent for the identification of mercaptans. It rapidly forms solids with all mercaptans thus far studied. The reagent is inexpensive, it is stable, and gives excellent yields of stable derivatives which are easily purified, having sharp melting points and definite crystalline structure. In no case was it necessary to heat the reactants for over ten minutes. The reagent is unique in that it forms solid sulfides that can be rapidly oxidized to the corresponding sulfones, thus ensuring complete identification in a remarkably short time.

[1] Wertheim, THIS JOURNAL, **51**, 3661 (1929).
[2] Bennett, *J. Chem. Soc.*, **121**, 2139 (1922).
[3] Schacht, *Ann.*, **129**, 1 (1864).
[4] Borgstrom, Ellis and Reid, THIS JOURNAL, **51**, 3649 (1929).
[5] Reid, Mackall and Miller, *ibid.*, **43**, 2108 (1921).

Experimental

Preparation of Sulfide.—The general procedure used to make the condensation products with 2,4-dinitrochlorobenzene was carried out as follows. 0.01 Mole of the mercaptan was added to 30 ml. of absolute alcohol in the case of liquid mercaptans; in the case of solid mercaptans, the smallest amount of hot alcohol necessary to dissolve it was used. The sodium mercaptide was made by adding 0.01 Mole of sodium hydroxide dissolved in 3 ml. of water to the mercaptan solution. 0.01 Mole of 2,4-dinitrochlorobenzene was dissolved in 10 ml. of absolute alcohol in a 100-ml. balloon flask and the alcoholic solution of the sodium mercaptide added to the flask containing the reagent. At this point many mercaptans react almost instantly, as shown by the generation of heat and the precipitation of the sulfide. To ensure complete reaction the mixture was refluxed on the steam-bath for ten minutes. The hot solution was quickly filtered, whereupon the sulfide crystallized in beautiful golden-yellow needles from the filtrate on cooling. The product was recrystallized from absolute alcohol until a constant melting point was obtained. As a general rule the melting point was not raised after one recrystallization except in the case of iso-mercaptans. It has been found best to use a slight excess of mercaptan. This prevents the formation of a reddish-brown solution caused by an excess of sodium hydroxide which might affect the purity of the final product.

The melting points of the sulfides are given in Table I. In certain cases the melting points of the sulfides are not far enough separated to ensure complete identification. Thus further to ensure the identity of the mercaptan, the sulfide was converted into the sulfone by oxidation with potassium permanganate in acid solution at room temperature.

TABLE I

DERIVATIVES OF MERCAPTANS WITH 2,4-DINITROCHLOROBENZENE

Mercaptan	M. p., °C. (corrected)	Analysis for sulfur, % Calcd.	Found	Mercaptan	M. p., °C. (corrected)	Analysis for sulfur, % Calcd.	Found
Methyl	128	14.97	14.84	Octyl	78	10.27	10.12
Ethyl	115	14.05	14.11	Nonyl	86	9.83	9.38
n-Propyl	81	13.25	13.36	Cetyl	91	7.60	7.50
Isopropyl	94.5	13.25	13.47	Thiophenol	121	11.57	11.71
n-Butyl	66	12.51	12.54	*p*-Thiocresol	103	11.05	11.05
Isobutyl	76	12.51	12.76	Benzyl	130	11.05	11.08
n-Amyl	80	11.87	11.76	Phenylethyl	89.5	10.54	10.51
Isoamyl	59	11.87	11.88	Thienyl	119	22.61	22.72
Hexyl	74	11.28	11.02	Furfural	130	11.43	11.68
Heptyl	82	10.75	10.88	Biphenyl	146	9.09	9.21

Preparation of Sulfone.—0.01 mole of the sulfide was dissolved in just enough glacial acetic acid to put it into solution. In cases of difficultly soluble sulfides, solution may be facilitated by gentle warming. The solution was treated with 50% excess of the calculated amount of potassium permanganate dissolved in thirty times its weight of water to form the sulfone. The permanganate was added, with shaking, as fast as it was decolorized. Some of the less soluble sulfides have a tendency to precipitate on addition of the aqueous solution of the permanganate. In such cases, a slight excess of acid should be added to keep it in solution and ensure complete oxidation. When all the permanganate had been added, the excess was removed by treating with a solution of sulfurous acid at room temperature, avoiding an excess of the reagent. In most cases the sulfone occurs in the form of a colorless precipitate at this point. In cases where it is only incompletely precipitated at this point, two or three volumes of cracked ice is added.

The sulfone is filtered, dried and recrystallized from absolute alcohol. In a few cases purification was facilitated by the use of charcoal. Usually one recrystallization is sufficient. The sulfones are colorless needles having sharp melting points. Data on these compounds are found in Table II.

TABLE II

SULFONES OF 2,4-DINITROPHENYL THIOETHERS

Sulfone	M. p., °C. (corrected)	Analysis for sulfur, % Calcd.	Found	Sulfone	M. p., °C. (corrected)	Analysis for sulfur, % Calcd.	Found
Methyl	189.5	13.00	12.87	Heptyl	101	9.69	9.81
Ethyl	160	12.30	12.67	Octyl	98	9.30	9.31
n-Propyl	127.5	11.68	11.78	Nonyl	92	8.93	8.86
Isopropyl	140.5	11.68	11.55	Phenyl	161	10.38	10.40
n-Butyl	92	11.11	11.05	*p*-Cresyl	189.5	9.93	9.89
Isobutyl	105.5	11.11	11.04	Benzyl	182.5	9.93	9.90
n-Amyl	83	10.59	10.70	Phenylethyl	133.4	9.52	9.56
Isoamyl	95	10.59	10.69	Thienyl	143	20.38	20.14
Hexyl	97	10.12	10.22	Biphenyl	170	8.33	8.61

The above sulfides and sulfones may be prepared on a much smaller scale using 0.001 molar quantities of the reactants in the proportionate amounts of solvent and carrying out the reactions in test-tubes. Where only enough of the sulfide or sulfone is desired for a melting point, this procedure may be followed with gratifying results. Under ordinary conditions, the conversion of the mercaptan into the sulfide and thence into the sulfone may be accomplished in twenty to twenty-five minutes, although with a higher degree of technique it is possible to carry out the reactions in even shorter time.

Summary

1. 2,4-Dinitrochlorobenzene readily reacts with sodium mercaptides to form alkyl and aryl dinitrophenyl thioethers.

2. The dinitrophenyl thioethers are easily oxidized to the corresponding sulfones by potassium permanganate in acetic acid solution.

3. 2,4-Dinitrochlorobenzene is strongly recommended as a reagent for mercaptans.

CHAPEL HILL, NORTH CAROLINA
SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. XX. THE STRUCTURE OF TUBAIC ACID

BY H. L. HALLER AND F. B. LAFORGE

RECEIVED DECEMBER 24, 1931 PUBLISHED MAY 7, 1932

In a brief note recently published in THIS JOURNAL[1] it was reported that on catalytic hydrogenation tubaic acid ($C_{12}H_{12}O_4$) yields a mixture of dihydrotubaic ($C_{12}H_{14}O_4$) and tetrahydrotubaic ($C_{12}H_{16}O_4$) acids. The latter was stated to be 2,4-dihydroxy-3-isoamylbenzoic acid, and its relation to tubaic acid was indicated. The present paper presents the experimental evidence for these statements.

Tetrahydrotubaic acid is practically insoluble in cold chloroform, in alcoholic solution it gives a violet color with ferric chloride, and it is optically inactive. It readily forms a diacetyl derivative ($C_{16}H_{20}O_6$) and a monomethoxy acid ($C_{13}H_{18}O_4$). The monomethoxy acid resists further methylation. When heated to its melting point the tetrahydro acid loses carbon dioxide, forming an alkyl resorcinol.

The fact that tetrahydrotubaic acid is practically insoluble in cold chloroform, in contrast to tubaic and dihydrotubaic acids, which are soluble in this solvent, suggests that tetrahydrotubaic acid contains an hydroxyl group para to the carboxyl group, as para hydroxy acids are insoluble in cold chloroform.[2]

Tubaic acid is optically active, but isotubaic acid ($C_{12}H_{12}O_4$), which differs from tubaic acid in the position of a double bond, is optically inactive. The resolution of dihydroisotubaic acid,[3] the levo form of which is identical with dihydrotubaic acid, proves that the isomerization of tubaic acid to isotubaic acid is due to the migration of a hydrogen atom originally attached to an asymmetric carbon atom. It follows, therefore, that the asymmetric carbon atom in tubaic acid possesses one hydrogen atom.

Tetrahydrotubaic acid also is optically inactive, indicating that one of its hydroxyl groups is formed by the opening of a ring containing an indifferent oxygen atom which is attached on one side to an asymmetric carbon atom. The disappearance of the optical activity of tubaic acid on drastic hydrogenation, as well as in the isomerization of tubaic to isotubaic acid, is proof that tubaic acid has but one asymmetric center.

Diacetyltetrahydrotubaic acid, which is easily obtained from the tetrahydro acid by the action of acetic anhydride and sodium acetate, is converted into a monoacetyltetrahydrotubaic acid when it is refluxed in a

[1] Haller and LaForge, THIS JOURNAL, **53**, 4460 (1931).

[2] Meyer, "Analyse und Konstitutionsermittlung organischen Verbindungen," 5th ed., 1931, p. 418.

[3] Butenandt and Hildebrandt, *Ann.*, **477**, 245 (1930); Takei, Koide and Miyajima, *Ber.*, **63**, 1369 (1930).

solution of potassium acetate in absolute alcohol. In alcoholic solution this monoacetyl derivative gives a violet color with ferric chloride.

On methylation of tetrahydrotubaic acid with dimethyl sulfate and dilute alkali, its monomethoxymethyl ester is obtained, which is readily saponified, to the monomethoxy acid ($C_{13}H_{18}O_4$).

Attempts to methylate the second hydroxyl group were unsuccessful.

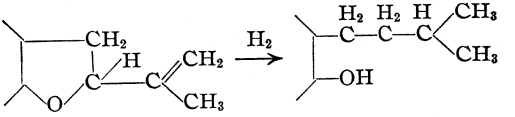
The fact that one of the hydroxyl groups in tetrahydrotubaic acid resists methylation, and the corresponding acetyl derivative is easily saponified, indicates that the hydroxyl group involved is di-ortho substituted.

When heated to its melting point the tetrahydro acid loses carbon dioxide and is converted into a crystalline substance ($C_{11}H_{16}O_2$) which gives the characteristic reactions of resorcinol.

That only one alkyl group is present in the diphenol and that this group is an isoamyl group is shown by the following facts: on oxidation with potassium permanganate tubaic acid yields only acetic acid, whereas under the same conditions isotubaic and dihydrotubaic acids give isobutyric acid.

Takei[4] isolated isovaleric acid by alkali fusion of isotubanol ($C_{11}H_{12}O_2$), (decarboxylated isotubaic acid), and he also demonstrated the presence of the isoallyl group in tubaic acid. On ozonization of tubanol methyl ether, he obtained a methyl ether methyl ketone, which on oxidation with hypoiodide yielded an iodine-containing carboxylic acid that had one carbon atom less than the methyl ketone. We have ozonized the acetyl derivative of tubaic acid ($C_{14}H_{14}O_5$) and obtained from the ozonide a product which analyzes for a compound of formula $C_{13}H_{12}O_6$ and gives the reactions of a methyl ketone.

From the foregoing facts it follows that grouping A is present in tubaic acid and that on drastic hydrogenation it is changed to grouping B.



A B

Tubaic acid and all rotenone derivatives which are converted by hydrogenation into phenolic compounds therefore contain the grouping $-\overset{1}{O}-\overset{2}{CH}-\overset{3}{C}=\overset{4}{CH_2}$. This grouping is comparable with that of a conjugated system, and hydrogenation takes place with the opening of the ether ring.[5] This reaction is explained by the assumption that a 1,4-addition of hydrogen (at —O— and C_4) first takes place, followed by the formation of the double linkage at 2,3. This double linkage is further reduced in the formation of

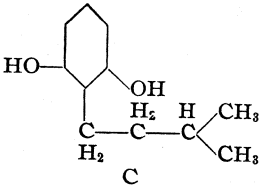
[4] Takei, Koide and Miyajima, *Ber.*, **63**, 1369 (1930).

[5] Schöpf, *Ann.*, **452**, 237 (1927); **483**, 157 (1930).

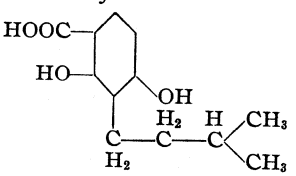
tetrahydrotubaic and dihydrorotenonic acids, but remains unsaturated in rotenonic acid, which therefore contains the grouping $-\overset{H_2}{C}-\overset{H}{C}=C(CH_3)_2$. This reaction is analogous to the formation of β-tetrahydrodesoxycodeine from desoxycodeine-C.[6]

The position of the alkyl group in the resorcinol derivative is either 2, 4 or 5 (formula C). Position 4 is excluded because this alkyl resorcinol is known. Its melting point is 62–62.5°, while the compound obtained from tetrahydrotubaic acid melts at 85°. Position 5 is excluded because alkyl groups meta to the hydroxyl groups in resorcinol do not give a fluorescein reaction. Also it is more probable that the two linkages on the benzene nucleus of the original oxide ring of tubaic acid are ortho to each other rather than meta, and therefore the alkyl group and the hydroxyl group in tetrahydrotubaic acid are also ortho to each other rather than meta. It follows, therefore, that the alkyl group occupies position 2.

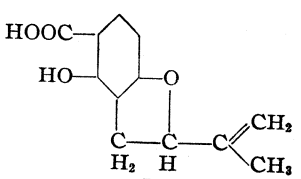
The behavior of the tetrahydro acid indicates that the carboxyl group is ortho to one of the hydroxyl groups and para to the other. Tetrahydrotubaic acid is best represented by D.



C



D



E

Structure E, which satisfactorily accounts for all the known facts, is now proposed for tubaic acid.

The relation of tubaic acid to rotenone has been discussed in a previous paper.[7]

Tubaic acid was considered to be a secondary decomposition product because at that time[8] the rotenone molecule was supposed to contain a lactone group and also because it was difficult to account otherwise for the failure to obtain tubaic acid when rotenone derivatives were oxidized with hydrogen peroxide, as tubaic acid is stable to this oxidizing agent. The fact that no tubaic acid is obtained is satisfactorily accounted for, however, with consideration of the observation of Dakin[9] on the oxidation of hydroxy aromatic aldehydes and ketones with hydrogen peroxide. Dakin has shown that hydroxy aromatic aldehydes and ketones in which the free hydroxyl group is in the ortho or para position to the aldehyde or ketone group, are oxidized by hydrogen peroxide with the formation of polyphenols. *No substituted benzoic acid is formed in the reaction.*

[6] Small and Cohen, THIS JOURNAL, **53**, 2221 (1931).

[7] LaForge and Haller, *ibid.*, **54**, 810 (1932).

[8] LaForge, Haller and Smith, *ibid.*, **53**, 4400 (1931).

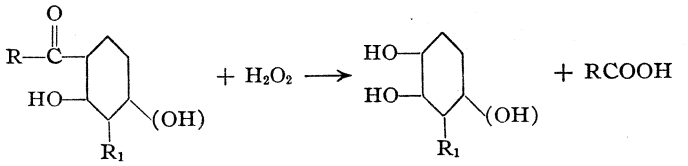
[9] Dakin, *Am. Chem. J.*, **42**, 477 (1909).

Most of the rotenone derivatives which are cleaved by hydrogen peroxide possess an hydroxyl group ortho to the carbonyl group, and in some cases an hydroxyl group is present in both the ortho and para positions.

Derrisic acid has an hydroxyl group ortho to the carbonyl group. In this case, on oxidation with hydrogen peroxide, cleavage takes place between the carbonyl group and the benzene ring with the formation of derric acid and probably a catechol derivative, which is for the most part oxidized further by the excess of peroxide. No tubaic acid is formed in the process.

Dehydrodihydrorotenonic acid possesses an hydroxyl group para to the carbonyl group. In the oxidation of this compound hydrolysis of the ortho (ether) oxygen linkage probably takes place first, and oxidation then proceeds with the formation of risic acid.

Methylderritolic and dihydrorotenolic acids have a hydroxyl group in the ortho position as well as in the para position, and oxidation takes place without the formation of tubaic acid. On the other hand such compounds as rotenone itself and rotenonic acid are not cleaved by hydrogen peroxide. These reactions are illustrated as follows



Experimental

Tetrahydrotubaic Acid (2,4-Dihydroxy-3-isoamylbenzoic Acid).—One gram of tubaic acid dissolved in 25 cc. of ethyl acetate was reduced with hydrogen at 48 lb. pressure, with 0.5 g. of freshly prepared reduced platinum oxide as catalyst. The reduction was allowed to proceed for two hours. The solution was filtered and concentrated to dryness on the steam-bath. The mixture of dihydro and tetrahydrotubaic acid was dissolved in 95% alcohol. The solution, heated to boiling, was diluted with an equal volume of hot water and filtered through charcoal.

The crystals which deposited on cooling were found to be pure dihydrotubaic acid. On concentration of the filtrate a second crop of crystals was obtained. This was filtered off, dried and then washed several times with cold chloroform. The remaining substance was crystallized from 20% alcohol. It can also be recrystallized from benzene, chloroform or toluene. It melted at 206° with decomposition, and was optically inactive. The yield was about 0.1 g.

Anal. Subs., 0.0822, 0.0806: CO_2, 0.1931, 0.1903; H_2O, 0.0529, 0.0526. Calcd. for $C_{12}H_{16}O_4$: C, 64.25; H, 7.20. Found: C, 64.07, 64.40; H, 7.20, 7.30. *Titration.* Subs., 0.0297: 1.34 cc. of *N*/10 KOH. Calcd. mol. wt., 224.13. Found: acid equivalent, 222.

Attempts were made to increase the yield of tetrahydrotubaic acid by the use of different solvents as well as by the addition of pinene to the ethyl acetate solution. Ethyl alcohol (95%) and glacial acetic acid were employed as solvents, but in all cases there was no appreciable increase in the amount of tetrahydrotubaic acid formed.

Diacetyltetrahydrotubaic Acid.—Two-tenths gram of tetrahydrotubaic acid was

refluxed in 5 cc. of acetic anhydride and 0.2 g. of anhydrous sodium acetate for one hour. After most of the solvent had been removed by distillation, water was added. The precipitated oil soon crystallized. The substance was filtered off and dissolved in 10 cc. of 95% alcohol. After the solution had been refluxed for one hour, it was diluted with an equal volume of hot water, filtered through charcoal and allowed to crystallize. The diacetate which separated melted at 143°. The yield was 0.18 g.

Anal.[10] Subs. (mg.), 3.052, 3.997: CO_2, 7.020, 9.151; H_2O, 1.750, 2.335. Calcd. for $C_{16}H_{20}O_6$: C, 62.31; H, 6.52. Found: C, 62.73, 62.44; H, 6.42, 6.54. *Titration.* Subs., 0.0338: 2.15 cc. of *N*/20 KOH. Calcd. mol. wt., 308.16. Found: acid equivalent, 314.

To 0.0338 g. of the diacetyltetrahydrotubaic acid was added 8.75 cc. of *N*/20 KOH. The solution was heated on the steam-bath for one-half hour, cooled and the excess of alkali was titrated with *N*/10 hydrochloric acid. The reaction required 3.28 cc. of *N*/20 potassium hydroxide; calcd. for 2 acetyl: 3.28 cc. of *N*/20 KOH.

Monoacetyltetrahydrotubaic Acid.—Two-tenths gram of diacetyltetrahydrotubaic acid was dissolved in 2 cc. of absolute alcohol containing 0.2 g. of potassium acetate. The solution was refluxed for one hour and then diluted with an equal volume of water. After the solution had cooled, 0.5 cc. of 20% sulfuric acid was added carefully. The substance, which separated immediately, was crystalline. It was filtered off, washed with water and dried. The yield was 0.08 g. It melted at 156°. In alcoholic solution it gave a purple color with ferric chloride.

Anal. Subs. (mg.), 3.223, 3.406: CO_2, 7.452, 7.869; H_2O, 1.991, 2.068. Calcd. for $C_{14}H_{18}O_5$: C, 63.13; H, 6.82. Found: C, 63.07, 63.01; H, 6.91, 6.79. *Titration.* Subs., 0.0270: 2.05 cc. of *N*/20 KOH. Calcd. mol. wt., 266.14. Found: acid equivalent, 264.

To 0.0270 g. of monoacetyl tetrahydrotubaic acid was added 5.20 cc. of *N*/20 potassium hydroxide. The solution was heated on the steam-bath for one-half hour. It was then cooled, and the excess alkali was titrated with *N*/10 hydrochloric acid. The reaction required 4.07 cc. of *N*/20 potassium hydroxide. Calcd. for 1 acetyl, 4.07 cc. of *N*/20 KOH. On addition of excess acid to the solution obtained above, tetrahydrotubaic acid separated. It was identified by its melting point.

Methyltetrahydrotubaic Acid (2-Hydroxy-4-methoxy-3-isoamylbenzoic Acid).—To 0.2 g. of tetrahydrotubaic acid dissolved in 5 cc. of 5% potassium hydroxide solution was added 0.5 cc. of dimethyl sulfate. The solution was frequently shaken and was kept alkaline by further addition of alkali. After two hours, it was acidified with dilute sulfuric acid. The precipitate was filtered off, washed with water and then refluxed in 95% alcohol to which had been added 1 cc. of 5% potassium hydroxide in order to saponify any ester that had formed. The solution was concentrated, diluted with an equal volume of water, filtered through charcoal and acidified with dilute sulfuric acid. On cooling, the methoxy acid separated. The yield was 0.18 g. The acid was recrystallized from dilute alcohol. It can also be crystallized from benzene. It melted at 156°. In alcoholic solution it gave a purple color with ferric chloride.

Anal. Subs. (mg.), 3.387, 4.300: CO_2, 8.110, 10.357; H_2O, 2.300, 2.939. Calcd. for $C_{13}H_{18}O_4$: C, 65.51; H, 7.62. Found: C, 65.30, 65.69; H, 7.60, 7.65.

An attempt was made to methylate the second hydroxyl group by using a large excess of methyl iodide and silver oxide and also with methyl iodide and potassium carbonate, but in each case unchanged starting material was recovered.

[10] We are indebted to Mr. J. R. Spies of this Division for the microcombustions reported in this paper.

Tetrahydrotubanol (2-Isoamylresorcinol).—Five-tenths gram of tetrahydrotubaic acid was heated in a Wood's metal bath at 215–225° for about five minutes. When the evolution of carbon dioxide, which took place vigorously at first, had ceased, the remaining reddish liquid was distilled under reduced pressure. On cooling it readily crystallized. The substance was recrystallized from chloroform–petroleum ether. It can also be recrystallized from benzene–petroleum ether (b. p. 37–75°). It melted at 85°.

Anal. Subs. (mg.), 3.560, 3.936: CO_2, 9.504, 10.521; H_2O, 2.807, 3.115. Calcd. for $C_{11}H_{16}O_2$: C, 73.28; H, 8.95. Found: C, 72.81, 72.90; H, 8.82, 8.86.

The compound gave a precipitate with bromine water, and a cherry red color with Millon's reagent. With Lieberman's reagent, an intense blue color was obtained. This soon turned quite dark and on dilution with water the color practically disappeared. There was no change on addition of alkali. When the substance was dissolved in chloroform, and a small piece of potassium hydroxide was added a rose-red color was slowly produced around the edges of the potassium hydroxide (Guareschi–Lustgarten reagent).[11] In alcoholic solution no color test was obtained with ferric chloride, but in aqueous solution a purplish-blue color was formed with this reagent. The color disappeared on addition of sodium bicarbonate.

With formaldehyde and sulfuric acid a red ring slightly tinged with violet was obtained.[12] After fusion with phthalic anhydride and a drop of concentrated sulfuric acid, the diluted solution became red with a green fluorescence when excess alkali was added.

Ozonization of Acetyltubaic Acid.—A stream of ozonized oxygen was passed into a solution of 1 g. of acetyltubaic acid in 15 cc. of chloroform for four hours Most of the chloroform was then removed by distillation. Water was added to the remaining sirup, and the solution was boiled for fifteen minutes. It was then cooled, and extracted with ether. The ether extract was dried over sodium sulfate. On removal of the ether, the substance readily crystallized. It was washed with isopropyl ether and recrystallized from a solution of 20% acetic acid—80% butyl ether. The yield was 0.2 g. It melted at 145°.

Anal. Subs., 0.0832, 0.0845: CO_2, 0.1784, 0.1834; H_2O, 0.0356, 0.0358. Calcd. for $C_{13}H_{12}O_6$: C, 59.07; H, 4.58. Found: C, 58.48, 59.19; H, 4.79, 4.74. Subs., 0.0475: cc. of $N/10$ KOH, 1.87. Calcd. mol. wt., 264.1. Found: acid equivalent, 254.

The substance reduced Fehling's solution, and with sodium hydroxide and iodine it gave iodoform. The same compound was obtained when acetyltubaic acid was ozonized in glacial acetic acid.

Conversion of Tetrahydrotubanol to Tetrahydrotubaic Acid.—Two-tenths gram of tetrahydrotubanol was refluxed in 50 cc. of a saturated solution of sodium bicarbonate for half an hour. The solution was cooled, filtered and acidified with dilute sulfuric acid. The precipitate was filtered off, washed with water and dried. It was then twice recrystallized from benzene. It melted at 206° and was identified as tetrahydrotubaic acid.

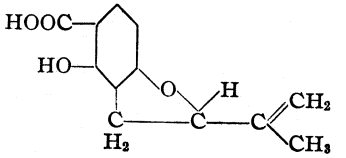
Summary

Tubaic acid is reduced by hydrogenation with platinum oxide catalyst to a mixture of dihydro and tetrahydrotubaic acid.

Tetrahydrotubaic acid is 2,4-dihydroxy-3-isoamylbenzoic acid, and tubaic acid is represented by the formula

[11] Rosenthaler, "Der Nachweis organischen Verbindungen," 1923, p. 240.

[12] Mulliken, "Identification of Pure Organic Compounds," 1908, Vol. I, p. 24.



An explanation of the mechanism of the oxidation of rotenone derivatives by hydrogen peroxide is given.

The behavior of tubaic acid on hydrogenation is analogous to that of desoxycodeine-C. Both contain the same groupings and both give tetrahydrophenols under the same conditions.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

QUINAZOLINES. III. THE INTERACTION OF ANILINE WITH 2-CHLORO-4-ALKOXYQUINAZOLINES AND 2-CHLORO-4-KETODIHYDROQUINAZOLINE

BY N. A. LANGE AND F. E. SHEIBLEY

RECEIVED DECEMBER 26, 1931 PUBLISHED MAY 7, 1932

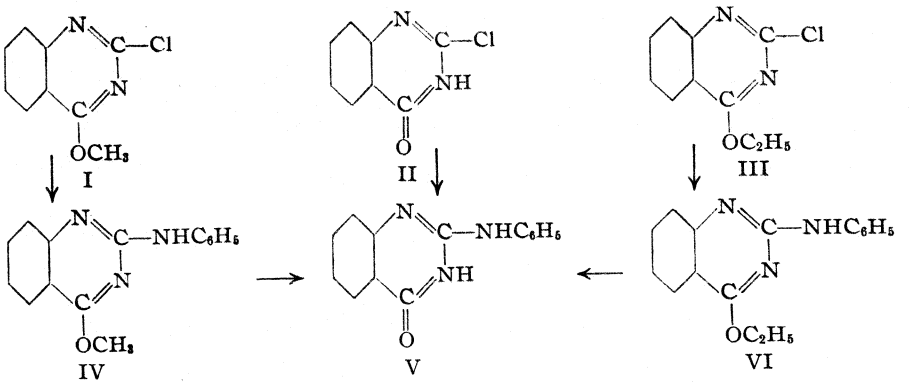
When 2,4-dichloroquinazoline in alcohol is boiled with sodium acetate, a compound with properties and a composition corresponding to a chloroketodihydroquinazoline is always found among the reaction products. In an earlier communication it was stated that by analogy with the similarly formed 2-chloro-4-alkoxyquinazolines this substance was most likely 2-chloro-4-ketodihydroquinazoline but that attempts to confirm this view by converting it into the known 4-ketodihydroquinazoline and 2-ethoxy-4-ketodihydroquinazoline were unsuccessful.[1]

The ease with which aniline replaces both of the chlorine atoms of 2,4-dichloroquinazoline with phenylamino groups suggested the possibility of transforming 2-chloro-4-alkoxyquinazolines into 2-anilino derivatives. By treating 2-chloro-4-methoxyquinazoline (I) and 2-chloro-4-ethoxyquinazoline (III) with aniline in alcohol, hydrochlorides of 2-anilino-4-methoxyquinazoline (IV) and 2-anilino-4-ethoxyquinazoline (VI), respectively, are obtained. These last, on hydrolysis with dilute hydrochloric acid in the presence of aniline, or simply on heating, when the elements of an alkyl chloride are evolved, revert to the known 2-anilino-4-ketodihydroquinazoline (V), a compound which results directly when the previously mentioned chloroketo compound is treated with an alcoholic solution of aniline, and thus identifies the latter as 2-chloro-4-ketodihydroquinazoline (II).

A confirmation of the orientation of the halogen and alkoxy groups in the chloro-alkoxy derivatives arrived at in a previous paper[2] is afforded

[1] Lange and Sheibley, THIS JOURNAL, **53**, 3871 (1931).

[2] Lange, Roush and Asbeck, *ibid.*, **52**, 3696 (1930).



by the identity of (V) with a specimen of 2-anilino-4-ketodihydroquinazoline prepared according to the method of previous investigators.[3] When phenylpseudomethylthiourea in ethereal solution was treated with anthranilic acid, what appeared to be an anthranilate of the base was precipitated. This product on fusion evolved methyl mercaptan, and the residue, treated with sodium hydroxide, yielded a product identical with (V) in every respect.

The free bases, 2-anilino-4-methoxyquinazoline (IV) and 2-anilino-4-ethoxyquinazoline (VI), are readily obtained from their hydrochlorides by treatment with sodium alcoholates. They are colorless, easily soluble substances, crystallizing in plates rather than the usual needles common to this class of compounds, and form characteristic salts.

All melting points given in this paper are corrected.

Experimental Part

Preparation of $\overline{N{=}COCH_3C_6H_4N{=}C}NHC_6H_5\cdot HCl$, 2-Anilino-4-methoxyquinazoline Hydrochloride.—A mixture of 2.2 g. of 2-chloro-4-methoxyquinazoline and 1.2 g. of aniline was dissolved in 30 cc. of alcohol and the solution boiled under a reflux condenser on a steam-bath for one hour. The condenser was then removed and the alcohol allowed to evaporate until the total volume of the reaction mixture was about 10 cc. This was cooled slightly, or till crystallization just began, and diluted with 40 cc. of ether; the precipitated mass was disintegrated with a glass rod, filtered and washed with ether, and weighed 3.1 g. A crystallization from alcohol yielded 1.8 g. of slightly yellow needles (m. p. 152°); further purification was effected by recrystallizing from methyl alcohol containing a few drops of concentrated hydrochloric acid, when colorless needles of 2-anilino-4-methoxyquinazoline hydrochloride, melting around 160° (decomp.), were obtained.

Similarly when 1.5 g. of chloromethoxyquinazoline and 0.9 g. of aniline in 25 cc. of methyl alcohol were heated, 0.75 g. of a precipitate (m. p. 295°, and probably impure benzoylene urea) separated after the first half hour of heating and was removed by filtration. Concentration of the filtrate and precipitation with ether as outlined above yielded 1.6 g. of crude 2-anilino-4-methoxyquinazoline hydrochloride.

[3] Wheeler, Johnson and McFarland, THIS JOURNAL, 25, 797 (1903).

This compound is soluble in alcohol, methyl alcohol or acetone, and insoluble in water, concentrated hydrochloric acid or ether. Its melting point was found to vary slightly but in general pure specimens melted within the range 158–161° (decomp. and foaming with loss of methyl chloride), the melts then solidifying and remelting within a range of 255–260°, the latter melting points being identical with those of impure specimens of 2-anilino-4-ketodihydroquinazoline (V). Recrystallization from ethyl alcohol gave blunt needles or prisms somewhat shorter than the crystals from methyl alcoholic solutions but of identical melting point.

A platinichloride was immediately precipitated on mixing hot methyl alcoholic solutions of the hydrochloride and platinic chloride. Washed with hot methyl alcohol and dried, it formed a granular, light orange, micro-crystalline mass, softening with decomposition at 225–230°, and soluble only in chlorohydrin. It ignites without melting.

Anal. Calcd. for $C_{15}H_{14}ON_3Cl$: C, 62.59; H, 4.91; N, 14.61; Cl, 12.33. Found: C, 62.94; H, 5.00; N, 14.51; Cl, 12.21. Calcd. for $(C_{15}H_{14}ON_3Cl)_2PtCl_4 \cdot H_2O$: Pt, 20.99. Found: Pt, 20.89, 20.98.

Preparation of $\overline{N{=}COC_2H_5C_6H_4N{=}C}NHC_6H_5 \cdot HCl$, 2-Anilino-4-ethoxyquinazoline Hydrochloride.—This compound was obtained in the same manner as the anilinomethoxy derivative just described: 1.5 g. of 2-chloro-4-ethoxyquinazoline and 0.75 g. of aniline in 25 cc. of alcohol yielded 2.0 g. of crude precipitated product. A crystallization from alcohol gave 1.2 g. of fine needles (m. p. 161°); further recrystallizations from alcohol containing a few drops of hydrochloric acid resulted in colorless needles melting around 170°. The solubilities of this substance are the same as those of the analogous anilinomethoxy salt. Its melting point was also variable, pure specimens fusing within the range 168–171° with evolution of ethyl chloride and consequent solidifying and remelting around 259° due to the formation of 2-anilino-4-ketodihydroquinazoline (V). When kept at 40° for a day or so, these hydrochlorides often acquire a yellow color without any apparent change in composition.

Anal. Calcd. for $C_{16}H_{16}ON_3Cl$: C, 63.66; H, 5.35; Cl, 11.76. Found: C, 64.32; H, 5.27; Cl, 12.00.

Hydrolysis of the Hydrochlorides of 2-Anilino-4-methoxyquinazoline (IV) and 2-Anilino-4-ethoxyquinazoline (VI) to 2-Anilino-4-ketodihydroquinazoline (V).—Originally, instead of precipitating it with ether as described above, 2-anilino-4-ethoxyquinazoline hydrochloride was isolated by pouring the alcoholic reaction mixture into water, adding sufficient hydrochloric acid to dissolve the droplets of excess aniline, and removing the precipitated product by filtration. This method was later found to promote an appreciable hydrolysis; moreover, when it was attempted to prepare the anilino-methoxyquinazoline hydrochloride in the same way, the precipitation of the product was incomplete and on warming hydrolysis ensued. However, when pure specimens of these hydrochlorides were boiled with alcoholic hydrochloric acid and even with concentrated aqueous hydrochloric acid, aniline being absent, no appreciable hydrolysis was observed; this stability toward hydrolysis is in contrast to the non-basic and easily hydrolyzed 2-chloro-4-alkoxyquinazolines which even on standing soon decompose into benzoylene urea. Because of this property, the following procedure was finally adopted. One-half gram of 2-anilino-4-methoxyquinazoline hydrochloride with 5 cc. of alcohol, 10 drops of hydrochloric acid, 2 drops of aniline and 10 cc. of water was slowly taken to dryness on a steam-bath over a period of three hours or longer. The residue was washed with hot water and dissolved in normal sodium hydroxide, the solution diluted, filtered and precipitated from the hot solution by the addition of acetic acid. The white precipitate of 2-anilino-4-ketodihydroquinazoline thus obtained was washed with hot water

and dried, m. p. 261°. A similar treatment of 2-anilino-4-ethoxyquinazoline hydrochloride gave the same product, also in a practically theoretical yield, m. p. 261°.

Preparation of 2-Anilino-4-ketodihydroquinazoline (V) from 2-Chloro-4-ketodihydroquinazoline (II).—One and seventy-five hundredths grams of chloroketodihydroquinazoline and 1.0 g. of aniline were dissolved in 50 cc. of alcohol and the solution warmed on a steam-bath. A precipitate began to separate after the first few minutes of heating; at the end of two and one-half hours the mixture was cooled, diluted with 60 cc. of ether, and the precipitate filtered, washed with ether and dried. The 1.9 g. of material thus obtained was dissolved in hot normal sodium hydroxide and precipitated from the hot solution with acetic acid in the usual manner; this precipitate was filtered, washed with hot water and dried. It crystallized from an alcoholic solution to which water had been added in the form of tiny snow white rosets of minute needles, m. p. 261°. The compound is sparingly soluble in alcohol, acetone or methyl alcohol, and crystallizes in the same minute needles from all three solvents. It is insoluble in ether or ammonia but soluble in sodium hydroxide or concentrated sulfuric acid. For analysis, drying at temperatures above 100° was necessary in order to remove 2–3% of moisture which adhered to the material crystallized from dilute alcohol.

Anal. Calcd. for $C_{14}H_{11}ON_3$: C, 70.85; H, 4.68. Found: C, 70.80; H, 4.84.

Preparation of 2-Anilino-4-ketodihydroquinazoline (V) from Phenylpseudomethylthiourea.[3]—Ten grams of the hydroiodide of phenylpseudomethylthiourea[4] was dissolved in ether and converted into the free base by shaking with an aqueous solution of sodium carbonate. The ethereal layer, washed three times with water, was treated with 5 g. of anthranilic acid, when a slight evolution of heat occurred and 8.5 g. of a precipitate, m. p. 118°, and evidently an anthranilate of the base, soon separated. This product after filtering from the ether and drying was heated in an oil-bath at 120–130° for three hours; methyl mercaptan was evolved and a red glassy melt remained. Several extractions of this with boiling alcohol removed the viscous red material; the residue was dissolved in twice normal sodium hydroxide, filtered and precipitated with acetic acid as before. The dried precipitate was dissolved by prolonged boiling in alcohol and crystallization effected by diluting with water; m. p. 261°.

Melting points of mixtures of this product with the same compound obtained by the other three methods of preparation (*i. e.*, hydrolysis of the two anilino-alkoxy derivatives and the product of condensation of chloroketodihydroquinazoline with aniline) showed no depression. A mixture composed of samples from each of the products from the four methods of preparation melted at 261°.

Anal. Calcd. for $C_{14}H_{11}ON_3$: C, 70.85; H, 4.68. Found: C, 70.70; H, 4.78.

Preparation of 2-Anilino-4-methoxyquinazoline (IV).—To 0.4 g. of sodium dissolved in 40 cc. of methyl alcohol was added 1.9 g. of 2-anilino-4-methoxyquinazoline hydrochloride and the solution warmed slightly until a considerable quantity of sodium chloride began to separate. After standing overnight the mixture was poured into 100 cc. of water, when a white opaque suspension resulted. This began to crystallize immediately and within three hours the separation was complete. The crystalline product was filtered, dried and amounted to 1.53 g. of the crude base. Recrystallization was effected from either methyl alcohol or a hot methyl alcoholic solution to which a little water was added, the separation being more nearly complete when the latter method was employed.

The compound forms small colorless glistening plates, m. p. 113°. It is soluble in alcohol, methyl alcohol, petroleum ether, acetone or ether and insoluble in water. Treatment with hydrochloric acid in methyl alcohol regenerated the hydrochloride salt

[4] Bertram, *Ber.*, **25**, 49 (1892).

described above. When hot alcoholic solutions of the base and picric acid were mixed, a flocculent yellow precipitate consisting of fine needles of the picrate separated. This was washed with water and recrystallized from alcohol, from which it slowly separates as fine, light yellow, feathery needles, m. p. 210°.

Anal. Calcd. for $C_{15}H_{13}ON_3$: C, 71.68; H, 5.22. Found: C, 72.08; H, 5.15.

Preparation of 2-Anilino-4-ethoxyquinazoline (VI).—This compound was prepared in essentially the same way as the methoxy derivative just described. Ethyl alcohol was employed and the coagulation of the precipitate obtained on pouring the mixture into water was a matter of days rather than hours. One gram of 2-anilino-4-ethoxyquinazoline hydrochloride and 0.3 g. of sodium in 25 cc. of alcohol gave 0.85 g. of the crude precipitated base, which was recrystallized from 50% alcohol.

This compound separates as colorless glistening plates, m. p. 110–111°, somewhat larger than the crystals of 2-anilino-4-methoxyquinazoline. Its solubilities are the same as those given for the last-named substance. Addition of hydrochloric acid regenerated the hydrochloride but attempts to form an addition product with methyl iodide were unsuccessful. The picrate, prepared in the manner outlined above, crystallized from alcohol in rosets of coarse yellow needles, m. p. 183°; glossy needles were obtained on slow evaporation of the solvent.

Anal. Calcd. for $C_{16}H_{15}ON_3$: C, 72.41; H, 5.70. Found: C, 72.67; H, 5.81.

Summary

Aniline has been found to react with 2-chloro-4-ketodihydroquinazoline and with 2-chloro-4-alkoxyquinazolines to yield 2-anilino-4-ketodihydroquinazoline and hydrochlorides of 2-anilino-4-alkoxyquinazolines, respectively. The constitutions of 2-chloro-4-alkoxyquinazolines and of 2-chloro-4-ketodihydroquinazoline are demonstrated by their conversion into the known 2-anilino-4-ketodihydroquinazoline. The following new compounds have been prepared: 2-anilino-4-methoxyquinazoline, 2-anilino-4-ethoxyquinazoline and their picrates and hydrochlorides.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRY INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

BETA-SULFHYDRYL-BETA-PHENYLPROPIOPHENONE

BY BEN H. NICOLET

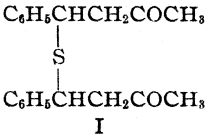
RECEIVED DECEMBER 26, 1931 PUBLISHED MAY 7, 1932

The writer has recently[1] had occasion to examine certain β-mercapto ketones of the type $C_6H_5CH(SR)CH_2COR'$, particularly from the point of view of their instability toward alkaline reagents. These ketones were readily obtained by the addition of mercaptans to α,β-unsaturated ketones in the presence of alkalies. To use β-*p*-tolylmercapto-β-phenylpropiophenone as an example, two characteristic reactions are as follows: (a) with alkali, easy loss of tolyl mercaptan to form benzalacetophenone; (b) with phenylhydrazine, easy loss of the mercaptan to form 1,3,5-triphenylpyrazoline.

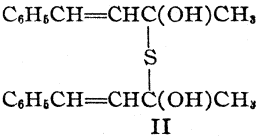
[1] Nicolet, THIS JOURNAL, 53, 3066 (1931).

An examination of the literature failed to reveal any β-sulfhydryl ketone ($RCH(SH)CH_2COR'$) described as such, but some work by Fromm attracted attention. He described[2] the condensation with benzalacetone and benzalacetophenone, of sodium sulfide, disulfide and hydrosulfide, processes which should presumably be analogous to the addition of alkali mercaptides to these same ketones. The structures he assigned to the products obtained were, however, rather unusual and require discussion here.

For his "duplobenzylideneacetone monosulfide," for example, he considered and rejected Formula I, and chose instead Formula II.



I



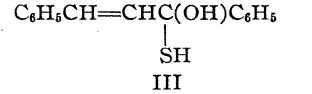
II

For this choice he gave two reasons: (a) the substance was readily decomposed by alkali, regenerating benzalacetone; (b) it reacted with phenylhydrazine, with loss of hydrogen sulfide, and yielded benzalacetonephenylhydrazone. One point against Formula II, he admitted, was that attempts at acylation gave no evidence of the presence of hydroxyl groups.

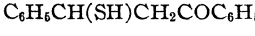
From what has been said of the β-mercapto ketones, all these properties are now seen to be entirely consistent with Formula I.

Fromm and Hubert[3] felt they had finally proved the correctness of a structure of type II, when they isolated the corresponding monosulfide of benzalacetophenone in three forms, each of which gave, on oxidation, a different sulfone. They interpreted these three sulfides as geometrical isomers of a substance analogous to that represented in Formula II. This result still requires investigation although Formula I presents the possibility of two geometrical isomers, with the possibility of additional enolized forms.

This discussion has been given to make clear the fact that Fromm's "benzalacetophenone hydrosulfide," to which he gave Formula III, is almost certainly β-sulfhydryl-β-phenylpropiophenone (IV), and, as such,



III



IV

the first β-sulfhydryl ketone. As might be expected, it loses hydrogen sulfide with ease, especially in the presence of alkali.

In attempting to prove the structure of this compound, Fromm found that on benzoylation it would take up only a single benzoyl group, which

[2] Fromm and Haas, *Ann.*, **394**, 290 (1912).

[3] Fromm and Hubert, *ibid.*, **394**, 301 (1912).

became attached to sulfur. No free hydroxyl group could be demonstrated. This same thiobenzoate has now been obtained by the direct addition of thiobenzoic acid to benzalacetophenone in alkaline solution. The thioacetate is similarly formed from thioacetic acid. Since these thio acids are even more similar than is hydrogen sulfide to the mercaptans whose addition has already been studied, the structures given by Fromm can scarcely be maintained.

Experimental Part

β-Sulfhydryl-β-phenylpropiophenone (IV).—The directions of Fromm and Hubert[3] were followed. A solution of the substance in dilute alcohol gave with lead acetate a test for sulfide after standing for only a few minutes at room temperature. The rate of sulfide formation increased rapidly on heating, or on the addition of small amounts of alkali.

β-Benzoylmercapto-β-phenylpropiophenone, $C_6H_5CH(SCOC_6H_5)CH_2COC_6H_5$.—A solution of two moles of potassium hydroxide in 10 parts of alcohol was saturated with hydrogen sulfide, then shaken with one mole of benzoyl chloride. When this solution (A) was added to one mole of benzalacetophenone, and 2 *N* sodium ethylate then added (0.5 cc. more than required to give a pink color with phenolphthalein) there was immediate evidence of reaction. After an hour, acidification with acetic acid gave almost entirely a sulfide (formula analogous to I) which proved to be identical with Fromm's β-duplobenzylideneacetophenone sulfide. This product also resulted when the benzoyl chloride was omitted.

When, however, solution A was acidified, the thiobenzoic acid extracted with ether, and this extract (after removal of ether) dissolved in alcohol and condensed with benzalacetophenone as described above (reaction time, however, ten hours at room temperature), the main product obtained was the benzoylmercapto derivative. After purification it melted at 123° and proved to be identical with the product obtained by Fromm when he benzoylated the mercaptan.

Anal. (Parr bomb). Calcd. for $C_{22}H_{18}O_2S$: S, 9.25. Found: S, 8.91, 9.02.

β-Acetylmercapto-β-phenylpropiophenone.—This substance was prepared as described for the benzoyl derivative, but with the use of thioacetic acid. It separated as a yellow oil, which solidified on cooling, and after purification from somewhat diluted alcohol melted at 75–77°. The crystals were still slightly yellow.

Anal. (Parr bomb). Calcd. for $C_{17}H_{16}O_2S$: S, 11.27. Found: S, 11.15.

Summary

Reasons have been given for the belief that Fromm's "benzalacetophenone hydrosulfide" is really β-sulfhydryl-β-phenylpropiophenone.

BELTSVILLE, MARYLAND

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS. XI. THE OXIDATION OF CIS-PHENYLBUTADIENE BY MEANS OF PERBENZOIC ACID[1]

BY IRVING E. MUSKAT AND MARGARET HERRMAN

RECEIVED DECEMBER 26, 1931 PUBLISHED MAY 7, 1932

Perbenzoic and peracetic acids have been used for some time to determine the degree of unsaturation and the rate of oxidation of olefinic compounds.[2] Of particular interest in our investigations is the work of Böeseken and Blumberger on the three isomeric phenylbutenes, $\Delta^{1,2}$-C_6H_5—CH=CH—CH_2—CH_3; $\Delta^{2,3}$-C_6H_5—CH_2—CH=CH—CH_3; $\Delta^{3,4}$-C_6H_5—CH_2—CH_2—CH=CH_2; and also on cinnamic acid and its methyl ester.[3] In the case of the phenylbutenes they found that the nearer the double bond is to the phenyl group the greater is the rate of oxidation; while both cinnamic acid and its ester are insensitive to oxidation by means of perbenzoic acid. From these facts they concluded that the phenyl group hastens the oxidation while the carboxyl group, at least when it is situated next to the double bond, hinders oxidation by means of perbenzoic acid.

Meerwein[4] has reported results similar to those on the phenylbutenes, from his study of the rate[5] of oxidation of safrole, isosafrole, eugenol and isoeugenol.

Arbuzov and Mikhailow[6] have studied the oxidation of unsaturated compounds by means of peracetic and perbenzoic acids and from their work have concluded that the first step in the oxidation reaction is the formation of cyclic oxides. Böeseken and his collaborators[7] recently have accepted this view although they had previously assumed that peracetic acid is absorbed by the double bond to give the monoacetate of the diol while perbenzoic acid oxidized the double bond directly to the cyclic oxide.

[1] Presented before the Organic Division of the American Chemical Society at its meeting in Buffalo, N. Y., 1931.

[2] Prileschajew, *Ber.*, **42**, 4811 (1909); *J. Russ. Phys.-Chem. Soc.*, **42**, 1387 (1910); **43**, 609 (1911); **44**, 613 (1912). For later work on detection and quantitative determination of unsaturation, see Bauer and Kutscher, *Chem. Umschau*, **32**, 57 (1925); Nametkin, *J. prakt. Chem.*, **112**, 169 (1926); *ibid.*, **115**, 56 (1927); Pummerer, *Ber.*, **62**, 1411 (1929); **62**, 2636 (1929); Smit, *Rec. trav. chim.*, **49**, 675 (1930); *ibid.*, **49**, 691 (1930). Derx, *ibid.*, **41**, 332 (1922).

[3] Böeseken and Blumberger, *ibid.*, **44**, 90 (1925); **45**, 838 (1926).

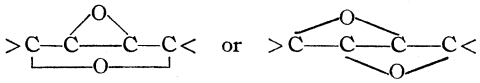
[4] Meerwein and co-workers, *J. prakt. Chem.*, **113**, 9 (1926).

[5] For work on velocities of oxidation by means of peracetic acid, see Charrier and Moggi, *Gazz. chim. ital.*, **57**, 736 (1928); Smit, *Rec. trav. chim.*, **49**, 686 (1930).

[6] Arbuzov and Mikhailow, *J. prakt. Chem.*, **127**, 1 (1930); *ibid.*, **127**, 92 (1930).

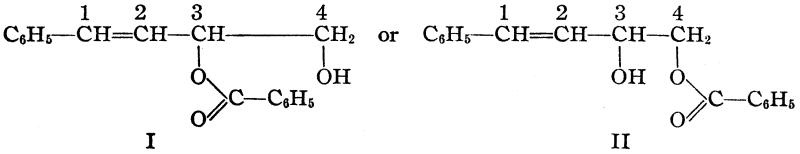
[7] Böeseken, *ibid.*, **131** (ii), 285 (1931).

Several authors[8] have studied the oxidation of unsaturated fatty acids and their esters by means of both peracetic and perbenzoic acids. It has been found that in the case of compounds containing two double bonds, whether conjugated or not, a dioxide is formed. Smit[8] found that in the case of 9,12-linolic acid the dioxide that is formed can be hydrolyzed but in the case of the conjugated 9,11-linolic acid the dioxide cannot be hydrolyzed. He suggests, therefore, these two possible structures for the dioxide of the conjugated compound.



In our work on the oxidation of *cis*-phenylbutadiene by means of perbenzoic acid, we have found that the products obtained depend largely on the temperature at which the reaction takes place. At 0° only one double bond of the unsaturated compound is attacked, while at 25° both double bonds are attacked.

If equimolar quantities of *cis*-phenylbutadiene and perbenzoic acid in chloroform solution are allowed to react at 0°, a white crystalline compound, m. p. 81–82°, is formed. This compound was proved by analysis to be an hydroxybenzoate formed by the addition of a mole of perbenzoic acid to one of the double bonds. The position of the remaining double bond was established by the isolation of the semicarbazone of benzaldehyde on ozonization. This proves, therefore, that the perbenzoic acid is absorbed in the 3,4-positions of phenylbutadiene and the benzoate must have one of the structures



I II

No effort was made to distinguish between these two possible structures, but on the basis of previous work[9] on the addition reactions of phenylbutadiene, and on the basis of the chemical reactions of the benzoate, which are to follow, structure I is favored.

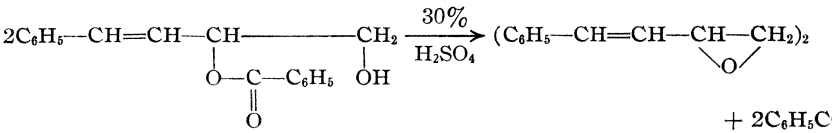
The fact that the double bond farther removed from the phenyl group is attacked more readily than is the one next to the phenyl group is in agreement with the previous work of Muskat and co-workers[9] but contrary to the conclusions drawn by Böeseken[3] and Meerwein.[4] Also,

[8] Bauer and Kutscher, *Chem. Umschau*, **325**, 57 (1925); *J. prakt. Chem.*, **122**, 201 (1929); Böeseken, *Chem. Abs.*, **23**, 4192 (1929); *Rec. trav. chim.*, **49**, 91 (1930); Smit, *ibid.*, **49**, 675 (1930); Braun, THIS JOURNAL, **52**, 3188 (1930).

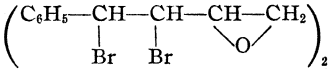
[9] Muskat and Huggins, *ibid.*, **51**, 2496 (1929); Muskat and Grimsley, *ibid.*, **52**, 1574 (1930).

the fact that a hydroxybenzoate was isolated as the *primary oxidation product* indicates that oxidation by means of perbenzoic acid occurs by the preliminary absorption of the peracid by the unsaturated compound, rather than through the formation of cyclic oxides as is postulated by Böeseken[7] and Arbuzov.[6]

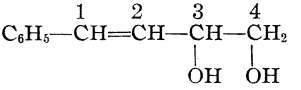
The benzoate was warmed on the steam-bath for twenty-four hours with 30% sulfuric acid. A white solid, m. p. 192°, and benzoic acid were isolated. The white solid, m. p. 192°, was found to be a dimer of phenylbutadiene monoxide. The position of the double bond was established by the isolation of benzoic acid on ozonization.



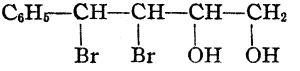
The fact that the double bond is not involved in the polymerization was established by the amount of benzoic acid isolated from ozonization—80% calculated on the basis of two moles of benzoic acid per mole of dimer—and confirmed by bromination. One mole of the dimer of phenylbutadiene monoxide absorbed two moles of bromine to give the tetrabromide of the dimer, m. p. 220°.



When the benzoate was treated with dilute sodium hydroxide solution at room temperature or even at 0°, it was hydrolyzed to a dihydroxy derivative of phenylbutadiene, a white crystalline material, m. p. 74°. When ozonized, the dihydroxy derivative yielded benzaldehyde, which proved the 3,4-structure of the dihydroxy derivative.

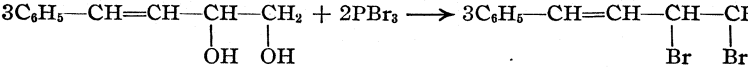


The dihydroxy derivative was dehydrated by means of phosphorus pentoxide in anhydrous ether solution and also by heating with 30% sulfuric acid in a bomb tube. The product obtained in each case was the dimer of phenylbutadiene monoxide, m. p. 192°. The dihydroxy derivative absorbed bromine to form 1,2-dibromo-3,4-dihydroxy-1-phenylbutane, m. p. 94°.



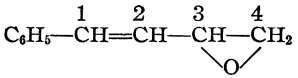
In order to link the work on oxidation with that on other addition reactions of conjugated compounds,[9] the dihydroxy derivative was treated

with phosphorus tribromide in anhydrous ether solution. The known 3,4-dibromide of phenylbutadiene, m. p. 94°, was obtained.



The tetrabromide of phenylbutadiene, m. p. 146°, was formed when the dihydroxy derivative of phenylbutadiene was treated with phosphorus pentabromide in anhydrous ether solution.

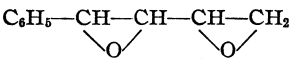
Accompanying the hydroxybenzoate there was always a small amount of the monoxide of phenylbutadiene, b. p. 88° under 1 mm. pressure. Again, the position of the double bond was determined by ozonization. Benzaldehyde was isolated as one of the ozonization products, which proved the 3,4-structure of the monoxide of phenylbutadiene.



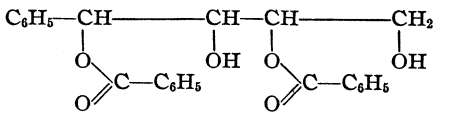
The monoxide yielded the dimer of phenylbutadiene monoxide when heated with 30% sulfuric acid on the steam-bath.

In addition to the small amounts of monoxide separated from the original reaction mixture, the monoxide has been obtained in very small amounts by heating the hydroxybenzoate at atmospheric pressure. Fifty per cent. of the theoretically possible yield of monoxide has been obtained by heating, in a bomb tube, the hydroxybenzoate in methyl alcohol solution containing a drop or two of dilute hydrochloric acid.

If two moles of perbenzoic acid are allowed to react with one mole of *cis*-phenylbutadiene at 25°, an oil is obtained from which two products were isolated: (1) an oil which distilled at 97° under 1 mm. pressure and was proved by analysis to be the dioxide of phenylbutadiene (A); and



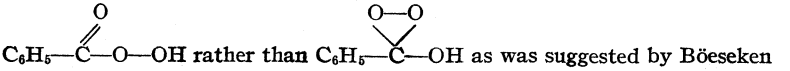
A



B

(2) a crystalline residue, m. p. 186°, which proved to be the dihydroxydibenzoate of phenylbutadiene. The most probable structure for this compound is (B).

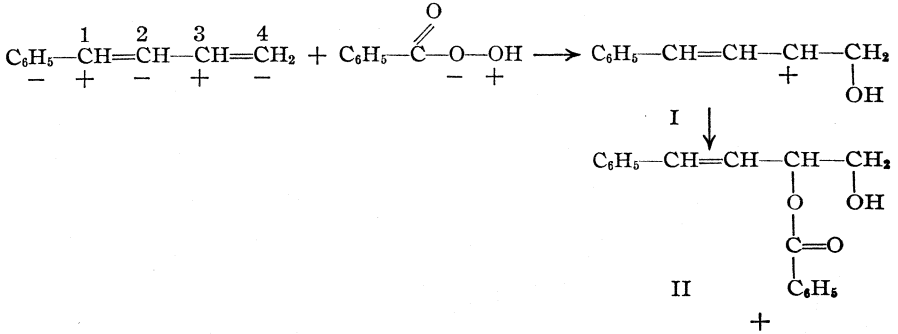
From the work presented above it is quite evident that the structure of perbenzoic acid must be represented as



The electronic structure of perbenzoic acid would then be indicated as



In a recent paper, Muskat and Northrup[11] developed a rather comprehensive electronic theory of the addition reactions of conjugated systems, which affords an explanation of the apparent discrepancies in the mode of addition of various reagents to such systems. According to this theory, "The addition of both components of the addendum to an ethylenic double bond does not occur simultaneously. It is more likely, as has been suggested by Stieglitz,[12] that the essential feature is the attraction of the positive substituting group to the negative carbon valencies." It follows as a direct corollary to this theory that the addition of different reagents to a particular conjugated compound should be fundamentally the same. Since we have previously found that the halogens and hypohalous acids—oxidizing agents—are added to phenylbutadiene in the 3,4-positions, we should expect that perbenzoic acid would also be added to—oxidize—the 3,4-double bond. The mechanism of the addition would then be represented as[11]



In the first step of the reaction the positive hydroxyl group (OH) is absorbed by the negative carbon atom (4) to give the intermediate I. The intermediate I would not undergo a 1,3-rearrangement to $C_6H_5—CH—CH=CH—CH_2OH$ due to the hindering influence of the phenyl group,[11] therefore the negative component, $C_6H_5—CO—O^-$, is absorbed by the 3-carbon atom to give hydroxybenzoate II. As has already been shown above, perbenzoic acid is actually absorbed by phenylbutadiene in the 3,4-positions to give the hydroxybenzoate II. At higher temperatures the 1,2-double bond is also attacked.

[10] The + and − signs as used here do not represent a complete transfer of electrons, but simply indicate that the atoms so marked are relatively electropositive or electronegative with respect to the atoms marked oppositely. See discussion by Muskat and Stieglitz to be published soon.

[11] Muskat and Northrup, THIS JOURNAL, **52**, 4043 (1930).

[12] Stieglitz, *ibid.*, **44**, 1304 (1922).

Experimental Part

Oxidation at Zero Degrees

Preparation of the Hydroxybenzoate of Phenylbutadiene.—A chloroform solution of perbenzoic acid was prepared by the method of Tiffeneau,[13] by treating benzoyl peroxide with sodium ethylate, liberating the perbenzoic acid with sulfuric acid and extracting with chloroform. The dried perbenzoic acid solution was cooled to 0° and slightly less than an equivalent amount of *cis*-phenylbutadiene was added, so that about a 2% excess of perbenzoic acid was present. The mixture was allowed to stand at 0° until oxidation was complete as indicated by iodimetric titration. The time required for this is about forty-eight hours. The chloroform was removed by means of suction without warming and the resulting pasty mass of crystals and oil was taken up in ether. The ether solution was shaken with iced 5% sodium hydroxide for half to three-quarters of an hour to remove the benzoic acid.[14] Care was taken to prevent heating and consequent increased hydrolysis when the alkali was added. The ether solution was separated, washed with water, dried over anhydrous sodium sulfate and filtered. The ether was removed by vaporization. A mass of flaky white crystals remained, which was recrystallized from hot low-boiling ligroin. The pure crystals melted at 81–82°.

Anal. Calcd. for $C_{17}H_{16}O_3$: H, 5.97; C, 76.12. Found: H, 5.63, 5.57; C, 76.16, 76.05. *Mol. wt.* Calcd. for $C_{17}H_{16}O_3$: mol. wt., 268. Found: mol. wt. (freezing point method), 273, 273.

The analysis proved this compound to be an hydroxybenzoate of phenylbutadiene. The hydroxybenzoate is very soluble in most organic solvents: benzene, chloroform, carbon tetrachloride, methyl and ethyl alcohol, ether, glacial acetic acid and acetone; but is only slightly soluble in hot low-boiling ligroin, and insoluble in water, dilute alkali and dilute acid. It may be recrystallized by adding ligroin to a benzene solution, water to a methyl alcohol solution, or by allowing the compound to crystallize slowly from hot low-boiling ligroin.

That the hydroxybenzoate was formed directly in the chloroform solution of perbenzoic acid and phenylbutadiene, and not from an esterification of the dihydroxy derivative which might have resulted from the hydrolysis of the oxide in alkaline solution, was established in two ways. (1) The pure monoxide was shaken with six times its equivalent of sodium benzoate in 5% sodium hydroxide solution for twenty-four hours, but no hydroxybenzoate could be detected. (2) The chloroform was evacuated from a portion of an original reaction mixture. The resulting pasty mass of solid, oil and a small amount of solvent was not treated with alkali but filtered to remove benzoic acid. As the filtration was very slow, more solvent was removed while filtering and crystals separated out in the filtrate. The first crystals obtained proved to be benzoic acid, but after several filtrations the crystals obtained, on recrystallization from hot low-boiling ligroin, melted at 79°, and a mixture with known hydroxybenzoate melted at 81.5°. This proved that the hydroxybenzoate was formed by the direct addition of perbenzoic acid to phenylbutadiene.

The hydroxybenzoate was subjected to ozonization in a manner entirely analogous to that described in previous work.[9] One gram of the hydroxybenzoate gave 0.08 g. of the semicarbazone of benzaldehyde and 0.63 g. of benzoic acid. This corresponds to an 82.5% yield of benzoic acid calculated on the basis of two moles of benzoic acid for each mole of hydroxybenzoate.

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 30.

[14] The chloroform solution of perbenzoic acid, prepared by the method of Tiffeneau, always contains benzoic acid.

The hydroxybenzoate did not absorb bromine readily at room temperature but on boiling with bromine in carbon tetrachloride solution a dibromide, m. p. 154–155°, was formed.

Anal. Calcd. for $C_{17}H_{16}O_3Br_2$: H, 3.74; C, 47.66; Br, 37.38. Found: H, 3.71, 3.79; C, 47.49, 47.69; Br, 37.38, 37.34.

The dibromide is soluble in benzene, ether, methyl and ethyl alcohol, chloroform and carbon tetrachloride, and only slightly soluble in hot low-boiling ligroin.

The Preparation of the Dimer of Phenylbutadiene Monoxide.—The hydroxybenzoate was heated on the steam-bath for twenty-four hours with 30% sulfuric acid. The reaction mixture was made alkaline and shaken with ether. A white crystalline product remained suspended in the ether layer. This was removed and carefully washed with ether. The pure crystals melted at 192°.

Anal. Calcd. for $(C_{10}H_{10}O)_2$: H, 6.90; C, 82.15. Found: H, 7.00, 7.33; C, 82.18, 82.35. *Mol. wt.* Calcd. for $(C_{10}H_{10}O)_2$: mol. wt., 292. Found: mol. wt. (boiling point method), 303, 307.

Benzoic acid was obtained when the alkaline extract was acidified.

The dimer of the monoxide is very slightly soluble in most of the common organic solvents but sufficiently soluble in warm ether to permit recrystallization from boiling ether.

The dimer of the monoxide of phenylbutadiene (0.45 g.), dissolved in chloroform, was ozonized for twelve hours. Most of the material (0.30 g.) was recovered unchanged, and 0.1 g. of benzoic acid, which represents 80% of the material decomposed by ozonization, was isolated.

The dimer of the monoxide of phenylbutadiene was brominated by boiling with bromine in chloroform solution. The product, a tetrabromide of the dimer, melts at 220°.

Anal. Calcd. for $C_{20}H_{20}O_2Br_4$: H, 3.27; C, 39.23. Found: H, 3.36, 3.34; C, 39.01, 39.17.

The Preparation of 3,4-Dihydroxyphenylbutadiene.—The hydroxybenzoate was shaken for three-quarters of an hour with twice the equivalent amount of 10% sodium hydroxide. The mixture was extracted with large volumes of ether, the ether extract dried over anhydrous sodium sulfate, the drying agent removed by filtration and the ether evaporated on the steam-bath. The oily mass that remained was taken up in hot benzene, from which solution crystals of the dihydroxy derivative, m. p. 74°, separated on cooling.

Anal. Calcd. for $C_{10}H_{12}O_2$: H, 7.37; C, 73.13. Found: H, 7.12, 7.38; C, 73.08, 73.11. *Mol. wt.* Calcd. for $C_{10}H_{12}O_2$: mol. wt., 164.1. Found: mol. wt. (boiling point method), 164.8, 167.5.

The dihydroxy derivative has also been obtained from the alkaline extract which results from the purification of the hydroxybenzoate.

The dihydroxy derivative is very soluble in hot benzene, soluble in methyl and ethyl alcohol, ether, acetone, warm acid and warm alkali, very slightly soluble in hot low-boiling ligroin and cold benzene, and insoluble in carbon tetrachloride, chloroform and cold water.

One gram of the dihydroxy derivative was ozonized for five hours. The ether extract of the alkaline solution yielded benzaldehyde, which was identified by the formation of its semicarbazone (0.2 g.). Benzoic acid (0.4 g.) was recovered from the alkaline extract. The amount of the two products isolated corresponds to 74.2% of the sample ozonized.

The dihydroxy derivative absorbed one mole of bromine in ligroin solution at room temperature to form a dibromide of the dihydroxy derivative, m. p. 94°.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2$: H, 3.73; C, 37.04. Found: H, 3.41, 3.68; C, 36.87, 36.97.

The dibromide of the dihydroxy derivative has the same melting point as the dibromide of phenylbutadiene but a mixture of the two melts at 86°. The dibromide of the dihydroxy derivative is much less soluble in ligroin than is the dibromide of phenylbutadiene.

The dihydroxy derivative was dissolved in ether and treated with five times the equivalent amount of phosphorus tribromide. The mixture was allowed to stand overnight, and the remaining phosphorus tribromide decomposed with ice. The water layer was extracted with ether and the ether was vaporized. The solid 3,4-dibromide of phenylbutadiene, m. p. 94°, remained. A mixture of this material with the known 3,4-dibromide of phenylbutadiene also melted at 94°. The dihydroxy derivative was treated in an analogous manner with phosphorus pentabromide. The product obtained was the tetrabromide of phenylbutadiene, m. p. 146°. A mixture with known tetrabromide of phenylbutadiene also melted at 146°.

The dihydroxy derivative was dehydrated to the dimer of the monoxide of phenylbutadiene, m. p. 192°, when an ether solution was treated with phosphorus pentoxide. The same product was isolated when the dihydroxy derivative was heated with 30% sulfuric acid at 100° for four hours in a bomb tube.

The Preparation of the Monoxide of Phenylbutadiene.—The hydroxybenzoate, in a methyl alcohol solution to which a few drops of dilute hydrochloric acid were added, was heated in a bomb tube at 120–130° for four to five hours. The methyl alcohol solution was then removed, a large volume of water was added and the mixture extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered and the major portion of the ether removed by means of suction. The remaining oil was distilled under reduced pressure. The fraction which distilled at 88° under 1 mm. pressure was a monoxide of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{10}O$: H, 6.90; C, 82.15. Found: H, 7.02, 7.29; C, 82.16, 82.36. *Mol. wt.* Calcd. for $C_{10}H_{10}O$: mol. wt., 146. Found: mol. wt. (freezing point method), 142.

One gram of the monoxide of phenylbutadiene was ozonized for five hours. Benzoic acid (0.45 g.) and the semicarbazone of benzaldehyde (0.13 g.) were isolated. The amount of the products isolated represented 65.4% of the material ozonized.

The monoxide of phenylbutadiene was warmed with 30% sulfuric acid on the steam-bath and the resulting viscous oil extracted with ether. From the ether extract the dimer of the monoxide of phenylbutadiene, m. p. 192°, was obtained.

The dry hydroxybenzoate was heated at atmospheric pressure for a short time. Most of the benzoate remained unchanged but a small amount of it was decomposed to the monoxide of phenylbutadiene and benzoic acid.

As has already been stated, small amounts of the monoxide oil always accompanied the hydroxybenzoate in the original reaction mixture.

Oxidation at 25°

Preparation of the Dioxidation Products.—*Cis*-phenylbutadiene was added to a slight excess of two equivalents of perbenzoic acid in chloroform solution at 25° and allowed to stand at that temperature until iodimetric titration indicated that no perbenzoic acid remained. This required eighteen to twenty hours. The resulting mixture was treated as described above for the hydroxybenzoate. The oil which remained

after the ether was removed was distilled under reduced pressure. At 97° under 1 mm. pressure a small amount of dioxide oil was distilled.

Anal. Calcd. for $C_{10}H_{10}O_2$: H, 6.22; C, 74.04. Found: H, 6.06, 6.35; C, 74.23, 74.06.

The residue in the distilling flask was taken up in benzene and the solution allowed to stand overnight. Crystals of a dihydroxydibenzoate separated and were recrystallized from hot benzene; their melting point after recrystallization was 186°.

Anal. Calcd. for $C_{24}H_{22}O_6$: H, 5.42; C, 70.93. Found: H, 5.20, 5.35; C, 70.86, 70.75. *Mol. wt.* Calcd. for $C_{24}H_{22}O_6$: mol. wt., 406. Found: mol. wt. (boiling point method), 371.4.

The dibenzoate is only slightly soluble in most organic solvents but moderately soluble in chloroform and acetone.

Summary

1. The 3,4-hydroxybenzoate of phenylbutadiene was isolated as the primary product of the oxidation of *cis*-phenylbutadiene by means of perbenzoic acid, when the reaction was carried out at 0°. A dihydroxybenzoate was obtained from the same reagents at 25°.

2. The 3,4-hydroxybenzoate of phenylbutadiene was hydrolyzed with alkali to 3,4-dihydroxyphenylbutadiene and derivatives of the dihydroxy compound were prepared.

3. The 3,4-hydroxybenzoate of phenylbutadiene was decomposed by acids to the monoxide or the dimer of the monoxide of phenylbutadiene. The product obtained depended upon the acid used and the conditions under which the reaction took place.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

ORIENTING INFLUENCES IN THE BENZENE RING. THE SULFONATION OF BENZOIC ACID[1]

BY JOHN S. REESE IV

RECEIVED DECEMBER 26, 1931 PUBLISHED MAY 7, 1932

Generally speaking, previous work has shown that benzoic acid may be sulfonated readily with strong sulfuric acid at high temperatures (*ca.* 200°) and by long duration of heating (two to twenty-four hours).[2] In this way about 90% of the product is the *m*-sulfobenzoic acid and the balance is the para isomer. Furthermore, Maarse,[2] incidental to a lengthy investigation of this problem, demonstrated that the meta isomer may be converted under the ordinary reaction conditions into the para isomer

[1] From a dissertation submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy. Presented before the Division of Organic Chemistry at the 82d Meeting of the American Chemical Society, Buffalo, N. Y., September, 1931.

[2] Maarse, *Rec. trav. chim.*, **33**, 207–238 (1914).

to the extent of about 15% although the reverse reaction was found to occur to about a three-fold greater degree. Now despite the fact that ortho substitution had been reported as totally absent and that metallic sulfates had no effect upon the sulfonation reaction, Dimroth and Schmaedel[3] have stated that the presence of mercuric sulfate not only increases the degree of sulfonation but also permits sulfonation in the ortho position to the extent of 5%.[3] Furthermore, Auger and Vary,[4] sulfonating variously in the presence of iodine, always obtained all three isomeric sulfobenzoic acids, of which the ortho amounted to only 1%. Although the main facts as presented above appear to be quite satisfactory, there are a few questions which are as yet unsettled. If the influence of such catalysts as iodine and mercuric sulfate is correctly reported, why does no ortho substitution normally take place? Why are the meta and para isomers so closely associated whereas all theories regarding orienting influences in the benzene ring demand that only the ortho and para isomers be so related? In addition, however, there were other rather interesting aspects which caused this problem to be investigated.

Without going thoroughly into the matter here, it was observed by the author from an extended study of the general problem of orienting influences that there was no substantial basis for the assumption that ortho and para substitution are closely related and opposed to meta substitution. Nevertheless it is perhaps well to present some of the more significant evidence for this particular point of view.

Although a superficial consideration of the evidence indicates that ortho substitution occurs frequently and perhaps always together with para substitution, whereas meta substitution takes place alone, a thorough examination will reveal that in nearly every case where an exhaustive study of the reaction products has been made, all three isomers are simultaneously formed.[5] Indeed it is rather the great number of cases in which all three isomers do occur that leads one to believe that such is the normal circumstance. True enough the amount of meta substitution is almost negligible in cases where para substitution predominates, yet when meta substitution is the greatest, para substitution is always less than the accompanying ortho substitution. Table I clearly illustrates the argument.

The above figures show that whether para or meta substitution predominates it is accompanied principally by ortho substitution and consequently that ortho is no more closely related to para than to meta substitu-

[3] Dimroth and Schmaedel, *Ber.*, **40**, 2411 (1907).

[4] Auger and Vary, *Compt. rend.*, **173**, 239 (1931).

[5] Exceptions are those such as sulfonation of nitrobenzene and benzene sulfonic acid where only the ortho isomer is absent. In such cases molecular rearrangements are known to occur and possibly account for the absence of the ortho isomer. Where halogenation gives no meta isomer, nitration shows that all three can occur as with toluene, and *vice versa* as with chlorobenzene.

TABLE I

NITRATION OF MONO-SUBSTITUTED BENZENES

Original substituent	% Meta	% Ortho	% Para
—COOH	76.5	22.3	1.2 [a]
—NO_2	90.9	8.1	1.0 [b]
—SO_3H	68.3	19.9	6.2 [c]
—CH_3	4.4	58.8	36.8 [d]
—OH	2.7	59.2	38 [e]
—Cl (bromination)	1.2	17.5	81.3 [f]
—$NH(CH_3CO)$	2.1	19.4	78.5 [g]

[a] Holleman, *Ber.*, **39**, 1716 (1906); [b] Holleman and de Bruyn, *Rec. trav. chim.*, **19**, 79 (1900); [c] Obermiller, *J. prakt. Chem.*, [2] **89**, 70 (1914); [d] Holleman and Vermeulen, *Chem. Centr.*, I, 1820 (1912); [e] Arnall, *J. Chem. Soc.*, **125**, 811 (1924); [f] Holleman and van der Linden, *Chem. Zentr.*, II, 640 (1910); [g] Arnall, *J. Soc. Chem. Ind.*, **48**, 1597 (1929).

tion. Furthermore, the simultaneous formation of the ortho and the meta isomer to the exclusion of the para is illustrated by the nitration of benzaldehyde in the presence of acetic anhydride, where 70% of the meta and 30% of the *o*-nitrobenzaldehyde were obtained.[6] Also, Reddelien[7] has found that benzaldehyde forms under certain conditions an addition compound with nitric acid which may be isolated as such. He then showed that this addition compound when treated with sulfuric acid alone yielded pure *m*-nitrobenzaldehyde. This, of course, was to be expected since the aldehyde group is a strong meta orienting substituent. But when this same benzaldehyde nitrate was treated with acetic anhydride in addition to the sulfuric acid, he obtained pure *p*-nitrobenzaldehyde. He further showed that whereas traces of *o*-nitrobenzaldehyde were found in both cases, at neither time did the para and the meta derivatives occur together. This experiment certainly suggests that ortho substitution takes place in any case and may be accompanied by either para or meta substitution. Generally, therefore, a careful examination of the evidence indicates that ortho substitution is midway between and equally related both to para and meta substitution and consequently this conception is proposed in place of the old and accepted one.

Closely related to the above aspect is the conclusion reached by Blanksma[8] that indirect substitution occurs only when the substituents —OH, —NH_2, —NHR, —OR or —CH_3 are present in the ring. Furthermore, it has been stated by Holleman[9] that indirect substitution leads always to ortho–para substitution, whereas direct substitution may lead to either ortho–para or to meta substitution, though principally to the latter. Now, as it

[6] Holleman, *Rec. trav. chim.*, **33**, 1 (1914).

[7] Reddelien, *J. prakt. Chem.*, **91**, 213 (1915); *Z. angew. Chem.*, **35**, 580 (1922).

[8] Blanksma, *Rec. trav. chim.*, **21**, 282 (1902).

[9] Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, p. 214.

will be shown later, it appears quite probable that in the sulfonation of benzoic acid, not only are ortho and meta substitution closely related but also they do occur indirectly. It may therefore be readily understood that the present investigation offered an opportunity to throw considerable light not only upon the specific question of the sulfonation of benzoic acid but also upon the general problem of orienting influences.

Indeed the available evidence suggests that the sulfonation of benzoic acid is actually an indirect substitution involving several intermediate compounds. Thus the first step, formation of an addition compound with the sulfuric acid, $C_6H_5COOH \cdot H_2SO_4$, is suggested by the work of Kendall and Carpenter,[10] who have indicated the existence of this addition compound by cryoscopic measurements. Support for a second step, a condensation under the influence of excess sulfuric acid to form benzoyl sulfuric acid, is given by Oppenheim's[11] preparation of this latter compound from benzoyl chloride and sulfuric acid. As for a third step, Oppenheim observed that benzoyl sulfuric acid changed on long standing to sulfobenzoic acid though he did not specify exactly which isomer. This scheme, involving an addition compound, a condensation, and a rearrangement, is by no means uncommon, being known to take place in the sulfonation of aniline,[12] and in all probability in the sulfonation of both toluene and phenol.[13] Yet these examples all lead to ortho and para substitution whereas no similar case of meta substitution is definitely known. Assuming, however, that with benzoic acid such a course of reaction does occur, a significant question is still unanswered. Are the para and meta isomers formed by a direct rearrangement of the benzoyl sulfuric acid or by a rearrangement of a possible intermediate *o*-sulfobenzoic acid? Indeed, it was the probability of the latter scheme that suggested the first step of this investigation.

Thus to determine whether the *o*-sulfobenzoic acid would rearrange to another isomer under the reaction conditions, it was heated with a large excess of concentrated sulfuric acid at 200° for various intervals of time from one-half hour to twelve hours. Upon recovering the potassium salts of the sulfobenzoic acids, they were converted to the hydroxybenzoic acids by fusion with caustic potash and the salicylic acid or the ortho isomer was removed from the mixture by extraction with chloroform in which it is readily soluble whereas the meta and para isomers are not. In this way it was found that the *o*-sulfobenzoic acid was converted solely to the meta isomer and the rate of conversion was thus quite readily determined.

[10] Kendall and Carpenter, THIS JOURNAL, **36**, 2500 (1914).

[11] Oppenheim, *Ber.*, **3**, 736 (1870).

[12] See Gattermann, "Die Praxis des org. Chemikers," 21st ed., 1928, pp. 156–157.

[13] Holleman and Caland, *Ber.*, **44**, 2509 (1911); Olsen and Goldstein, *Ind. Eng. Chem.*, **16**, 66 (1924); Baumann, *Ber.*, **11**, 1909 (1878).

Plotting the percentage of meta isomer against the time gave a regular curve approaching a maximum of about 85% in twelve hours (see Fig. 1). On the other hand, the natural logarithm of the concentration of the unchanged ortho isomer against the time gave a straight line as demanded by a monomolecular reaction. Similarly, with a view to the reported effect of mercuric sulfate on the sulfonation reaction, its influence upon this isomerization was studied. The rate of conversion was found to be greatly increased, over two-fold up to four hours of heating. The plot for the natural logarithm of unchanged ortho-isomer against the time was a straight line, suggesting as is very probable that this also is a mono-molecular reaction.

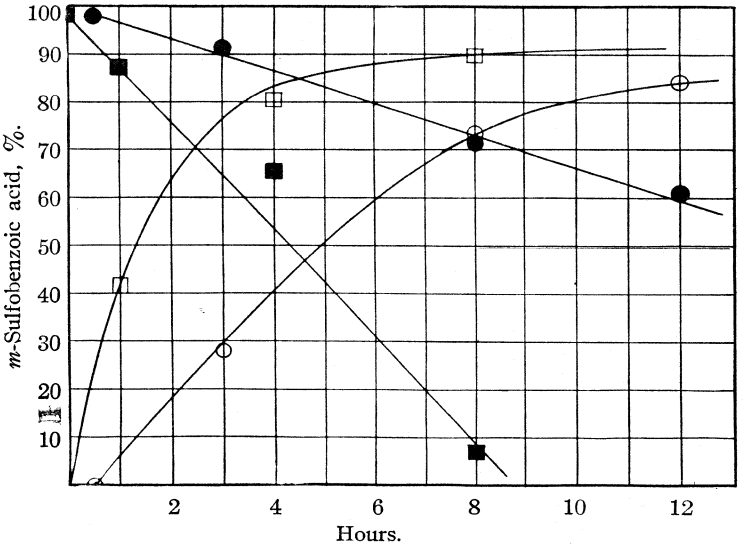


Fig. 1.—Isomerization of *o*-sulfobenzoic acid: ○ and ●, without mercuric sulfate; □ and ■, with mercuric sulfate; ● and ■, logarithm of the concentration of *o*-sulfobenzoic acid.

The sulfonation of benzoic acid at 200° both in the absence and presence of mercuric sulfate and for intervals of time where incomplete sulfonation would be obtained was then investigated. Thus, excepting that the unreacted benzoic acid was removed before fusion by extraction with ether of the solution of sulfobenzoic acids, an exactly similar procedure was followed and the degree of sulfonation and proportion of the isomers was determined for three, one, one-third and one-twelfth hours The following results were obtained.

It is perfectly apparent that the sulfonation proceeds far more rapidly than is indicated by previous work. Furthermore, the percentage of recovered product decreases markedly from the percentage of sulfonation

TABLE II

SULFONATION OF BENZOIC ACID AT 200°

Time, hrs.	% Sulfonation (reacted C_6H_5COOH)	Recovered product, %	Ortho substitution, % Without Hg	With Hg
3	99.1	98.3	6.3 (high)	2.3
1	95.5	93.3	5.8	3.8
1/3	81.0	75.0	14.3	7.3
1/12	35.9	11.6	[a]	[a]

[a] Only a trace of hydroxybenzoic acid was obtained (less than 0.05 g.).

calculated from the recovered unreacted benzoic acid. At five minutes practically no products were obtained although an apparent 36% sulfonation is definitely indicated. The same results are obtained when mercuric sulfate is present; but an explanation of this anomaly is suggested by a study of reaction velocity curves (see Fig. 2). The curve for the percent-

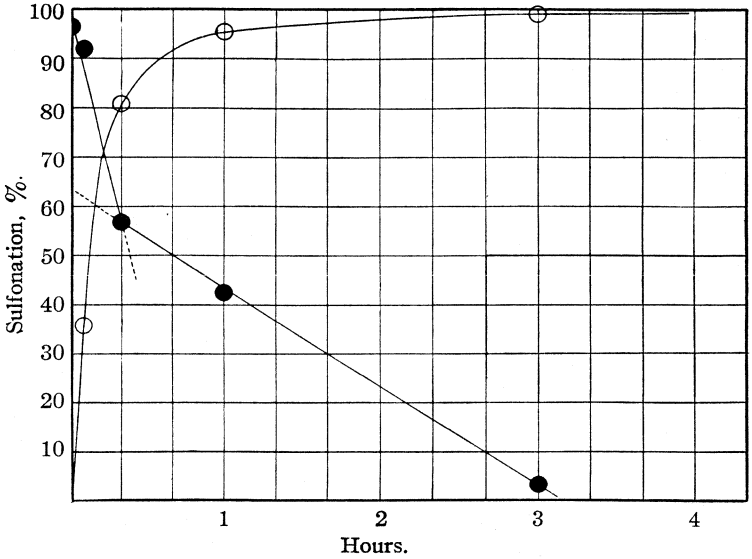


Fig. 2.—Sulfonation of benzoic acid at 200°: ○, % sulfonation; ●, logarithm of the concentration of unreacted benzoic acid.

age of sulfonation against time is perfectly regular in every respect. However, the plot of the natural logarithm of the concentration of the unreacted benzoic acid against the time breaks rather abruptly at about twenty minutes. This great divergence can scarcely be attributed to an experimental error since a correction in the direction of less sulfonation would only increase it, whereas a correction in the other direction would indicate entirely too great a degree of sulfonation to be on the curve at all. Furthermore, the twenty-minute sulfonation as well as the others also was virtually run in duplicate since it has been shown that the presence of

mercuric sulfate in no way influences the degree of sulfonation. To continue, therefore, from twenty minutes to three hours, the plot is a perfect straight line, whereas from zero time to twenty minutes it is probably a slight curve though of a decidedly greater slope. It is scarcely to be doubted therefore that this curve represents two distinct reactions, a primary and a subsequent one. Indeed, the most plausible explanation of these facts is that the portion of the curve up to twenty minutes represents the condensation of the addition compound to the benzoyl-sulfuric acid, possibly accomplished through the agency of the excess sulfuric acid. This part of the line though not indicated in this way should curve where the inevitable shading off to the subsequent reaction takes place. From this point on the straight line demands a monomolecular reaction and probably represents the isomerization of the benzoyl-sulfuric acid not to the *m*-sulfobenzoic acid but to the ortho isomer. An examination of the figures in the table above reveals this fact since increasingly larger amounts of the ortho isomer are formed in the absence of mercuric sulfate than in its presence as the sulfonation becomes more incomplete. This fact coupled with the effect of mercuric sulfate on the conversion of the ortho to the meta isomer indicates very strongly that the ortho isomer is actually an intermediate product.

The above interpretation presents a fairly probable picture of the reaction mechanism and agrees with the scheme as originally proposed. For a complete explanation, however, one must consider the formation of the para isomer. Yet recalling the work of Maarse,[2] it appears very likely that this isomer is formed by a conversion of the *m*-sulfobenzoic acid. Indeed, preliminary work on the isomerization of the meta isomer reveals that certainly no more than a trace of the ortho isomer is formed although it is perfectly obvious from a regular decrease in the melting point that a slight admixture of another substance is present in increasingly larger amounts as the time of heating is lengthened. Although further study would be of considerable interest, it is believed nevertheless that a clear insight into the nature of this reaction has already been obtained.

In conclusion, however, it may be added that the above work bears directly on the general problem of orienting influences. Not only has the total absence of ortho substitution as previously reported been explained, but it has also been shown that the apparently simultaneous and exclusive formation of the meta and para isomers is not an anomalous case. Indeed, considerable support has been obtained for a more nearly correct view of the relation of the three isomeric positions among di-substituted benzenes. Inasmuch as direct conversion of the ortho to the para isomer is a well-known reaction (see above) and since the present work offers the conversion of the ortho to the meta isomer as a complementary case, it at once appears that ortho substitution occupies a unique place between meta and

para substitution and is equally related to both. This proposition is obviously not in harmony with the long-accepted and time-honored point of view upon which has been based all previous and present hypotheses to explain orienting influences in the benzene ring. Closely related to this aspect of the question are the contention of Holleman and also the proposition of Blanksma concerning the occurrence of direct and indirect substitution. However, it is perfectly obvious from the present investigation that the sulfonation of benzoic acid, a well-recognized case of meta substitution, is actually an example of indirect substitution. Thus with all due respect to the weight and value of Holleman's opinion, this study is offered as support for ideas which are at complete variance with his. In addition it must be mentioned that in the light of this investigation, the work of Dimroth and Schmaedel as previously presented is apparently in error.

Experimental Part

Pure *o*-sulfobenzoic acid was prepared by the hydrolysis of *o*-sulfobenzoic anhydride, recrystallized from benzene (m. p. 118.5°).[14] Five grams of *o*-sulfobenzoic acid and 30 cc. of concentrated sulfuric acid (1.84) were placed in an Erlenmeyer flask and heated at 200° in an oil-bath for the desired length of time. The contents of the flask were run into about 800 cc. of water and neutralized with either barium carbonate or barium hydroxide. The precipitate of barium sulfate was removed by decantation of the supernatant liquid and filtration. The barium sulfate was also thoroughly washed with water, the washings being added to the filtrate. The residual barium contained in the filtrate as the barium salts of the sulfobenzoic acids was precipitated completely by addition of the necessary amount of dilute sulfuric acid. Following evaporation to about 400 cc. the barium sulfate was removed by decantation and filtration, the filtrate further evaporated, neutralized with potassium carbonate and finally evaporated to complete dryness.

The potassium salts of the sulfobenzoic acids thus obtained were powdered and fused with 10–15 g. of potassium hydroxide at 200–210° for two hours. The melt was completely dissolved with about 200 cc. of water and acidified with concentrated hydrochloric acid. The acidified solution was then extracted four times in a separatory funnel with 40 cc. of ether and the hydroxybenzoic acids obtained as a residue by distilling off the ether. This residue was then purified by extraction with absolute ether and a practically pure residue of hydroxybenzoic acids was thus obtained. Upon powdering this residue was extracted with 25 cc. of chloroform and removal of the chloroform by distillation gave a residue consisting of the *o*-hydroxybenzoic acid with a slight admixture of the meta isomer. The portion insoluble in chloroform was found to be practically pure *m*-hydroxybenzoic acid. The isomers were identified by their melting points and mixed melting points with the pure isomers. After weighing, a correction determined through solubility measurements was made for the admixture of the meta with the ortho isomer. It was thus readily possible to calculate the percentage conversion of the ortho to the *m*-sulfobenzoic acid.

The influence of mercuric sulfate was studied in a precisely similar fashion by the addition of 0.5 g. of this salt to the *o*-sulfobenzoic acid and sulfuric acid before heating.

The sulfonation of benzoic acid was investigated in the same way by dissolving 2.34

[14] Obtained from Hynson, Westcott and Dunning, Baltimore, Md., through the courtesy of Dr. F. Dunning.

g. of benzoic acid (C. P.) in 30 cc. of concentrated sulfuric acid (1.84) and heating for the desired length of time, namely, three, one, one-third and one-twelfth hours. The influence of mercuric sulfate was again studied in a similar fashion by the addition of 0.5 g. of this salt to the reaction mixture. The subsequent procedure was identical with the isomerization experiments except for the removal of the unreacted benzoic acid. This was accomplished by extraction of the acid solution of the sulfobenzoic acids reduced to about 125 cc. three times with 25 cc. of ether. The benzoic acid was weighed and the percentage sulfonation calculated. Finally, to identify absolutely the presence of the ortho isomer, the chloroform soluble residue was powdered in the small extraction flask, placed on a boiling water-bath with a water filled test-tube held in the neck of the flask through a stopper, and the ortho isomer or salicylic acid allowed to sublime onto the outside of the test-tube. In this way the presence of the least trace of salicylic acid could be demonstrated, since it gave the characteristic purple color in a water solution when tested with ferric chloride. This procedure was found necessary both on account of the slight amount of residue and since the melting point method was not completely satisfactory.

The percentage sulfonation was determined not only by the recovered unreacted benzoic acid, but also by the recovered potassium salts and the yield of hydroxybenzoic acids.

The author herewith desires to express his appreciation and gratitude for the generous advice and kindly encouragement of E. Emmet Reid, Professor of Chemistry, Johns Hopkins University.

Summary

A reaction scheme for the sulfonation of benzoic acid has been proposed and supported by a study of the isomerization of *o*-sulfobenzoic acid and the actual sulfonation reaction.

A new relation between ortho, meta and para substitution has been proposed and evidence from the sulfonation of benzoic acid added to that already found in the literature.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

ORGANIC REACTIONS WITH BORON FLUORIDE. I. THE PREPARATION OF ESTERS

BY H. D. HINTON AND J. A. NIEUWLAND

RECEIVED DECEMBER 31, 1931 PUBLISHED MAY 7, 1932

Bowlus and Nieuwland[1] found that boron fluoride united with acetic acid in the proportion of one mole of boron fluoride to two moles of acetic acid. This compound is a heavy liquid, fuming strongly in moist air. Analyses pointed to the formula $(CH_3COOH)_2BF_3$. By the use of this compound as a catalytic agent a series of esters has been prepared. The question as to whether the catalytic effect observed is due to the acid–boron fluoride compound, or to the reaction of this substance with some of the alcohol to form the boron fluoride compound, is at present unanswered.

[1] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

If the alcohol–boron fluoride compound is formed, it probably catalyzes the reaction in a manner similar to hydrochloric or sulfuric acid, since it has been shown to be acidic in character.[2]

Experimental

Ethyl Acetate.—The acetic acid–boron fluoride compound was prepared by passing boron fluoride gas into two moles of glacial acetic acid until one mole of the gas was absorbed. A flask containing 25 g. of acetic acid, 19.18 g. of ethyl alcohol and the catalyst was attached to a reflux condenser, and the contents refluxed from one to nine hours. After refluxing, a saturated solution of sodium carbonate was added to the reaction mixture, and the ester layer was recovered. A yield of 47–50% was obtained. An increase of the catalyst above one or two per cent. concentration did not increase the yield of ethyl acetate. One hour of refluxing produced practically the same amount of ester as a reflux of nine hours.[3]

Propyl Acetate.[4]—Seven grams of boron fluoride was passed into a mixture of 59.4 g. of propyl alcohol and 60 g. of glacial acetic acid. After refluxing for one-half hour, two layers separated, the top layer containing the ester. A yield of 53.5% of the ester was obtained.

Bowlus and Nieuwland[1] found that propionic acid absorbed one mole of boron fluoride to form a propionic acid–boron fluoride compound boiling at 62–63° (17 mm.). A series of alcohols was refluxed with this propionic acid–boron fluoride compound, each for forty-five minutes, and the corresponding esters were obtained in yields varying from 37 to 66%. Ethyl, propyl, *n*-butyl and *n*-amyl alcohols were used.[5]

Bowlus and Nieuwland did not report a butyric acid–boron fluoride compound. Experiments are being conducted in this Laboratory at the present time to determine if such a compound can be prepared. If it can, a series of esters with this compound should be possible. It was also found that on passing boron fluoride into aliphatic alcohols other than methyl and ethyl, hydrocarbon oils were obtained. After removing the oils, a strongly acid, fuming liquid similar to the methyl and ethyl alcohol solutions of boron fluoride was obtained. This solution, possibly, could be used as a catalytic agent for the preparation of esters. Experiments are being carried out in this Laboratory to find out if the reaction is possible. Evidence obtained up to the present time seems to prove that the above reaction can be used in the preparation of esters.

Summary

Using an acetic acid–boron fluoride compound, and a propionic acid–boron fluoride compound with a series of aliphatic alcohols, the corresponding series of esters has been prepared.

NOTRE DAME, INDIANA

[2] Nieuwland, Vogt and Foohey, THIS JOURNAL, **52**, 1018 (1930).

[3] Terre, "Thesis," University of Notre Dame, 1931.

[4] Seelinger, "Thesis," University of Notre Dame, 1932.

[5] Sullivan, "Thesis," University of Notre Dame, 1932.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

ORGANIC REACTIONS WITH BORON FLUORIDE. II. THE REARRANGEMENT OF ALKYL PHENYL ETHERS

BY F. J. SOWA, H. D. HINTON AND J. A. NIEUWLAND

RECEIVED DECEMBER 31, 1931 PUBLISHED MAY 7, 1932

The rearrangement of allyl and alkyl phenyl ethers has been a subject of study before and a number of isolated cases reported. Claisen,[1] by heating certain O-allyl aryl ethers to a high temperature, transformed them into the isomeric nuclei substituted phenols (C-allyl phenols). If the alkyl group is substituted for an allyl group, isomerization does not take place under the influence of heat, the presence of inorganic substances being necessary in most cases. In order to explain the substituted phenols obtained by Koenigs[2] and Schrauth and Quasebarth,[3] Niederl and Natelson[4] treated *o*-cresyl di-isobutyl ether with zinc chloride and hydrochloric acid. They also studied the action of a mixture of concentrated sulfuric acid and glacial acetic acid on saturated alkyl phenyl ethers, obtaining substituted phenols.

The purpose of the following investigation is to study the action of boron fluoride as an agent in the rearrangement of alkyl aryl ethers, to demonstrate its advantages as such, and to show that the products obtained by this method follow the same rules as those products obtained by Niederl and Natelson.[4]

Experimental

Preparation of Alkyl Phenyl Ethers.—One mole of phenol or cresol was weighed in a liter flask, fitted with a reflux condenser and a dropping funnel. A sufficient amount of water was added to 59 g. (excess) of potassium hydroxide to make a thick mixture, and this was added to the phenol. The whole mass was heated until solution became complete; 125 g. (excess) of isopropyl bromide was added slowly while shaking and warming. After all of the bromide was added, the contents were refluxed for one and a half hours, then poured into 400 cc. of water to dissolve the sodium bromide formed. The oil which separated at the top was washed several times with 10% sodium hydroxide solution, and finally with water. The oil was then dried over calcium chloride and distilled; yields from 50 to 75% were obtained.

Rearrangement of Alkyl Phenyl Ethers.—The procedure for the rearrangement of alkyl phenyl ethers is very nearly uniform and may be illustrated by the rearrangement of isopropyl *m*-cresyl ether.

Ninety-eight grams of the ether was weighed into a 500-cc. flask fitted with a three-holed stopper. A thermometer and an inlet tube were inserted below the surface of the liquid. Boron fluoride gas was passed into the ether. The preparation of the boron

[1] Claisen, *Ber.*, **45**, 357 (1912); *ibid.*, **58**, 275 (1925); *ibid.*, **59**, 2344 (1926); *Z. angew. Chem.*, **36**, 478 (1923).

[2] Koenigs and Carl, *Ber.*, **24**, 3889 (1891).

[3] Schrauth and Quasebarth, *ibid.*, **57**, 856 (1924).

[4] Niederl and Natelson, THIS JOURNAL, **53**, 1928 (1931).

fluoride followed the procedure of Bowlus and Nieuwland.[5] The temperature ranged from 27 to 43° when 3 g. of boron fluoride was added. The absorption was stopped and the mixture, which had a reddish tinge, was shaken vigorously. The temperature gradually went to 75° and the solution became dark red in color. The flask was heated to 85° and then shaken for about five minutes or allowed to stand overnight. At this point the boron fluoride gas was given off quantitatively. The solution was placed in a 500-cc. separatory funnel and washed once with 150 cc. of water and then extracted with 10% potassium hydroxide solution. The alkali insoluble layer was separated and washed with water until free from alkali. This was the reclaimed ether. The alkali-soluble layer was kept cool and neutralized with concentrated hydrochloric acid. Two layers appeared. The oily layer was separated and the other layer extracted with ether. The oily layer and the ether extract were combined. The ether was removed and the residue subjected to several fractionations.

From 98 g. of the ether, 63 g. of rearranged product was obtained, and 8 g. of the unchanged ether. This is a 64% yield based on the total quantity of ether used or 72% yield when the reclaimed ether is allowed to enter the calculations.

TABLE I

ETHERS AND REARRANGED PRODUCTS

	Ether	B. p., °C.,	d_4^{20}	n_D^{20}	Taken, g.
1	Isopropylphenyl	178	0.975	1.4992	34
2	Isopropyl *o*-cresyl	193	.953	1.5040	97
3	Isopropyl *m*-cresyl	194	.931	1.4959	98
4	Isopropyl *p*-cresyl	194	.927	1.4952	69

REARRANGED PRODUCTS

	Rearranged product	Yield, g.	%	B. p., °C.,	d_4^{25}	n_D^{25}
1	*o*-Isopropylphenol	22	64.7	212–214	1.004	1.5310
2	2-Methyl-4-isopropylphenol	51	52.5	231–235	0.975	1.5230
3	3-Methyl-x-isopropylphenol	63	64.2	230–236	.989	1.5275
4	4-Methyl-2-isopropylphenol	36	52.2	233–236	.982	1.5270

Discussion

The compounds which appear in this article have been reported previously and the structures established, with the exception of the rearranged product from isopropyl *m*-cresyl ether. The position of the isopropyl group in the ring is at present being studied at New York University.[4]

The method described in this investigation should be rather desirable: first, because never more than thirty-five minutes was required to complete a rearrangement studied. Second, the boron fluoride gas was easily recovered by merely heating the mixture. The temperature at which the gas was evolved varied from 85 to 150° for the different phenols. The amount of boron fluoride required for these rearrangements varied from one to five grams. When the minimum amount was used, warming and shaking were necessary.

The above ethers could be rearranged spontaneously by simply adding an excess of boron fluoride and allowing the temperature to rise.

[5] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

Solvents are not necessary but in certain cases they increase the yield. At present, an investigation regarding solvent action and the preparation of a series of new compounds of various phenolic ethers is being studied in this Laboratory.

Summary

1. The rearrangement of a series of alkyl phenyl ethers has been accomplished by the use of boron fluoride.

2. The boron fluoride can be recovered quantitatively.

3. The time required for the rearrangement of alkyl phenyl ethers has been materially shortened by this process.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE BEHAVIOR OF PHENYLACETONITRILE AND ALPHA-PHENYLBUTYRONITRILE WITH SODIUM ETHYLATE[1]

BY MARY M. RISING AND KEITH T. SWARTZ

RECEIVED DECEMBER 31, 1931 PUBLISHED MAY 7, 1932

The isolation of the pure alkali salts of phenylacetonitrile and α-phenylbutyronitrile by Rising in collaboration with Zee,[2a] Muskat and Lowe[2b] and Braun,[2c] and of the former nitrile by Upson,[3] involved the treatment of the nitriles with the alkali metals or amides. As observed by E. von Meyer[4] and his co-workers, and by Upson, and shown quantitatively for phenylacetonitrile by Braun, the reaction of the nitriles with sodium takes the course

$$2C_6H_5CH_2CN + 2\,Na \longrightarrow 2[C_6H_5CHCN]Na + 2H \quad (1)$$

$$[C_6H_5CHCN]Na + 2H \longrightarrow C_6H_5CH_3 + NaNC \quad (2)$$

The use of sodamide instead of sodium incurs no reduction of the salts.

It was suggested earlier[2a] that sodium ethylate might prove to be a useful reagent for obtaining the salts of these and other nitriles. The present paper describes the behavior of phenylacetonitrile and α-phenylbutyronitrile with solid sodium ethylate in dry boiling ether in an atmosphere of nitrogen. The ethylate has been used successfully in a great number of condensation reactions of nitriles[5] and the intermediate formation of sodium salts of the nitriles used is ordinarily assumed. We planned to

[1] The work here described forms part of the dissertation of K. T. Swartz, presented in partial fulfilment of requirements for the doctorate degree at the University of Chicago.

[2] (a) Rising and Zee, THIS JOURNAL, **49**, 541 (1927); **50**, 1699 (1928); (b) Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929); (c) Rising and Braun, *ibid.*, **52**, 1069 (1930).

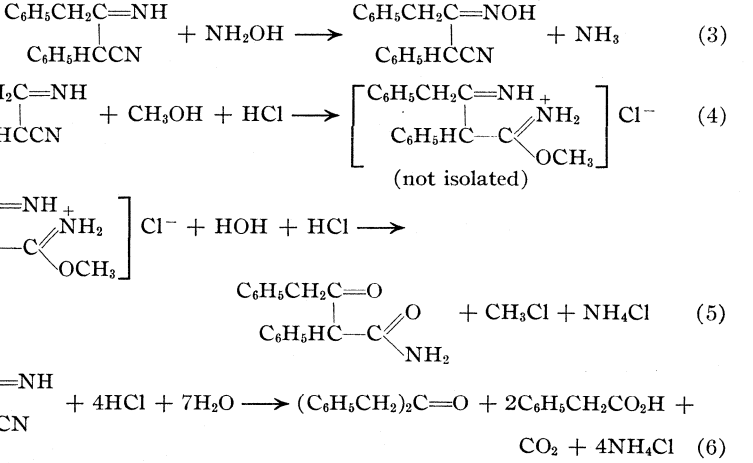
[3] Upson, Maxwell and Parmelee, *ibid.*, **52**, 1971 (1930).

[4] Wache, *J. prakt. Chem.*, **39**, 245 (1889); von Meyer, *ibid.*, **52**, 114 (1895), etc.

[5] Higson and Thorpe, *J. Chem. Soc.*, **89**, 1455 (1906); Avery and Upson, THIS JOURNAL, **30**, 600 (1908); Daughters, *ibid.*, **39**, 1927 (1917), and others.

isolate the intermediate products in the case of the nitriles studied, using the extremely delicate technique developed by Braun for handling the very unstable salts.

Under the conditions used by us phenylacetonitrile reacts with sodium ethylate to form a considerable quantity of sodium phenylacetonitrile. The major part of the salt formed apparently condenses with phenylacetonitrile to form a dimer of the nitrile, since the main product of the reaction is α,γ-phenyl-α-iminopropionitrile (dimolecular phenylacetonitrile), $C_6H_5CH_2C(=NH)CH(C_6H_5)CN$, formed in about 25% yield. Sodium phenylacetonitrile was not isolated from the reaction mixture, in which it is soluble, but its presence there, and the quantity formed, were shown by treatment of this mixture with benzyl bromide, and the resulting formation of α,β-diphenylpropionitrile, $C_6H_5CH(CH_2C_6H_5)CN$, in 11% yield. The identity of the dinitrile was established by the analytical data for the compound and by the results of molecular weight determination. Its structure was proved by its conversion into α,γ-diphenyl-β-oximinopropionitrile, $C_6H_5CH_2C(=NOH)CH(C_6H_5)CN$, and by a study of the products of hydrolysis of the dimer. The equations are



$$\begin{array}{c} C_6H_5CH_2C{=}NH \\ | \\ C_6H_5HCCN \end{array} + NH_2OH \longrightarrow \begin{array}{c} C_6H_5CH_2C{=}NOH \\ | \\ C_6H_5HCCN \end{array} + NH_3 \qquad (3)$$

$$\begin{array}{c} C_6H_5CH_2C{=}NH \\ | \\ C_6H_5HCCN \end{array} + CH_3OH + HCl \longrightarrow \left[\begin{array}{c} C_6H_5CH_2C{=}NH_+ \\ | \\ C_6H_5HC{-}C\begin{array}{l} \diagup NH_2 \\ \diagdown OCH_3 \end{array} \end{array}\right] Cl^- \qquad (4)$$

(not isolated)

$$\left[\begin{array}{c} C_6H_5CH_2C{=}NH_+ \\ | \\ C_6H_5HC{-}C\begin{array}{l} \diagup NH_2 \\ \diagdown OCH_3 \end{array} \end{array}\right] Cl^- + HOH + HCl \longrightarrow$$

$$\begin{array}{c} C_6H_5CH_2C{=}O \\ | \\ C_6H_5HC{-}C\begin{array}{l} \diagup O \\ \diagdown NH_2 \end{array} \end{array} + CH_3Cl + NH_4Cl \qquad (5)$$

$$2\begin{array}{c} C_6H_5CH_2C{=}NH \\ | \\ C_6H_5HCCN \end{array} + 4HCl + 7H_2O \longrightarrow (C_6H_5CH_2)_2C{=}O + 2C_6H_5CH_2CO_2H + CO_2 + 4NH_4Cl \qquad (6)$$

It is to be concluded that the mononitrile condenses with itself in the presence of sodium ethylate to form the dimer with intermediate formation of the sodium salt of the mononitrile. The product of this aldol-like condensation is the sodium salt of the dimer, which is hydrolyzed to the dinitrile. The dinitrile obtained, of molecular weight 228–235, was a viscous yellow oil of b. p. 222–223° (uncorr.) at 2.75 mm. pressure.

Dimolecular phenylacetonitrile was first prepared by von Meyer,[4] repeating the work of Wache,[4] who studied the behavior of phenylacetonitrile with sodium in ether but failed to isolate the dinitrile. Von Meyer obtained a viscous oil from which he prepared an oxime of melting point 107°,

identical with that obtained from cyanodibenzyl ketone, and he concluded that the oil was α,γ-phenyl-β-iminopropionitrile. Atkinson and Thorpe[6] prepared the dimolecular nitrile by heating phenylacetonitrile with sodium in alcohol for half an hour. Rondou[7] obtained the dinitrile by a Grignard reaction.

α-Phenylbutyronitrile, $C_6H_5CH(C_2H_5)CN$, was not found by us to condense with itself under the influence of sodium ethylate. After treatment of this nitrile with the ethylate under the conditions used in the case of phenylacetonitrile, 83% of the mononitrile used was recovered. The material obtained in a reaction of the nitrile with sodium ethylate was treated with methyl alcohol and hydrogen chloride. The products of this reaction were methyl α-phenylbutyrate and a substance of melting point 83° (uncorr.), thought to be α-phenylbutyramide. The amide, hitherto unprepared, was synthesized from α-phenylbutyryl chloride, also previously unknown, and ammonia, and showed a melting point of 83° (uncorr.). The melting point of a mixture of the amides obtained by the two methods was 83°. α-Phenylbutyryl chloride of boiling point 122–125° at 20 mm. was obtained from α-phenylbutyric acid and thionyl chloride.

The investigation of the tautomerism of nitriles is being continued in this Laboratory. An exhaustive study of the conductivities of a series of nitriles is under way, and the results of this work should form a logical basis for selection of nitriles best suited to the study of separation of tautomers. Salts of the nitriles with heavy metals are being studied.

Experimental

1. Reaction of Phenylacetonitrile with Sodium Ethylate in Ether.—Sodium ethylate was prepared from sodium (4 g.) and absolute alcohol (85 cc.) containing 25 cc. of absolute ether in an atmosphere of nitrogen. When the excess of liquids was removed by evaporation, solid white ethylate remained. Phenylacetonitrile (25.5 g., a 25% excess) was dropped into an ether suspension of sodium ethylate in an apparatus essentially like that used by Braun,[2c] the reaction being carried out in an atmosphere of nitrogen. All reagents and apparatus were dried thoroughly. The reaction mixture was refluxed for four hours, then 15 cc. of ligroin was added to precipitate unchanged sodium ethylate. The mixture was allowed to stand overnight; it was then filtered and three volumes of ligroin added to the filtrate to precipitate sodium phenylacetonitrile. The precipitate obtained consisted largely of sodium benzoate.[8] Sodium phenylaceto-

[6] Atkinson and Thorpe, *J. Chem. Soc.*, **89**, 1906 (1906).

[7] Rondou, *Bull. soc. chim. Belg.*, **31**, 231 (1922).

[8] It is evident that in spite of the precautions used to exclude air from apparatus and reagents some oxygen was present. The formation of benzoic acid may signify the breakdown of sodium phenylacetonitrile as follows

$$[C_6H_5CH{=}C{=}N]Na \longrightarrow C_6H_5CH{=} + NaNC{=}$$

as previously postulated by Rising and Zee,[2a] who obtained benzyl alcohol after the treatment of the salt with aqueous acid. Upson and Thompson [THIS JOURNAL, **44**, 186 (1922)] obtained benzoic acid from the impure salt following its exposure to air. A study of controlled oxidation of the salt will presently be made.

nitrile was not isolated from the reaction mixture, but its presence there was proved by treatment of a reaction mixture, obtained as just described, with benzyl bromide, whereupon α,β-diphenylpropionitrile was obtained in 11% yield. This nitrile melted at 57.5°[9] (uncorr.), boiled at 163–164° (uncorr.) at 3 mm., and yielded on hydrolysis α,β-diphenylpropionic acid of melting point 81–82° (uncorr.).[10]

2. α,γ-Diphenyl-β-iminopropionitrile. **Preparation.**—The reaction of phenylacetonitrile (46.1 g.) with sodium ethylate (prepared from 7.3 g. of sodium and 140 cc. of alcohol) was carried out as just described. The reaction solution was filtered after being refluxed, and was then treated with water; the ether layer was separated and dried over fused calcium chloride. The ether was then removed by evaporation and the oily residue was distilled, yielding about 16 g. of phenylacetonitrile and 10 g. (a 25% yield) of the dimolecular nitrile, of boiling point 222–223° (uncorr.) at 2.75 mm.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.00; H, 6.03; N, 11.97; mol. wt., 234. Found: C, 81.92, 82.11; H, 6.14, 6.28; N, 11.95, 12.06; mol. wt., 231 (av., benzene as solvent).

Proof of Structure. (a) **Oxime Formation.**—Treatment of the dinitrile in alcohol with hydroxylamine hydrochloride and barium carbonate (Equation 3) produced an oxime of melting point 106–107°, α,γ-diphenyl-β-oximinopropionitrile.[4,6]

(b) **Hydrolysis.**—(a′) Treatment of the dinitrile with concentrated hydrochloric acid[11] in a bomb tube at 150° for eight hours (Equation 6) produced carbon dioxide, phenylacetic acid[12] of melting point 76° (uncorr.), and dibenzyl ketone[13] of melting point 34–35° (uncorr.). The identity of the ketone was established by its conversion into dibenzyl ketone phenylhydrazone[14] of melting point 125–126° (uncorr.). (b′) Treatment of the dinitrile (4 g.) with methyl alcohol (15 cc.) and hydrogen chloride gas at 0° to saturation (Equations 4 and 5) produced phenylacetophenylacetamide of melting point 163.5–164° (uncorr.) formed in 76% yield.[11] The amide was hydrolyzed by alkali to phenylacetic acid of melting point 75–76° (uncorr.).

3. α-**Phenylbutyryl Chloride.**—α-Phenylbutyric acid (14 g.) was refluxed with thionyl chloride (100 g.) for eight hours. The reaction mixture was fractionated and the fraction of distillate, 14 g. in quantity, of boiling point 122–125° (uncorr.) at 20 mm. was found to be pure butyryl chloride, produced in 89.9% yield.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.42. Found: Cl, 19.37, 19.56.

4. α-**Phenylbutyramide.**—Dry ammonia was passed into an ether solution containing 5 g. of α-phenylbutyryl chloride. A vigorous reaction followed and precipitation of the amide and of ammonium chloride occurred. The precipitate was brought on a filter and washed with water to remove the salt. The amide was recrystallized from alcohol and melted at 83° (uncorr.). The yield was 63% of the theoretical. The amide was also obtained, together with methyl α-phenylbutyrate, by treatment of the crude reaction product, obtained by treatment of α-phenylbutyronitrile with sodium ethylate as previously described for phenylacetonitrile, and consisting largely of unchanged α-phenylbutyronitrile, with methyl alcohol and hydrogen chloride at 0°. The melting point of a mixture of the amide obtained by the two methods was 83° (uncorr.).

Anal. Calcd. for $C_{10}H_{13}ON$: C, 73.57; H, 8.03; N, 8.59. Found: C, 73.78, 73.63; H, 8.23, 8.23; N, 8.67, 8.80.

[9] Meyer, *Ber.*, **21**, 1308 (1888).

[10] Miller and Röhde, *ibid.*, **25**, 2018 (1892).

[11] Walther and Schickler, *J. prakt. Chem.*, **55**, 350 (1897).

[12] Möller and Strecker, *Ann.*, **113**, 64 (1860).

[13] Stobbe, Russwurm and Schulz, *ibid.*, **308**, 175 (1899).

[14] Francis, *J. Chem. Soc.*, **75**, 868 (1899).

Summary

1. Under the conditions used by us sodium ethylate is not a useful reagent for obtaining the sodium salt of phenylacetonitrile.

2. A considerable quantity of sodium phenylacetonitrile is undoubtedly formed in the reaction of the nitrile with sodium ethylate but much of the salt condenses with the mononitrile to form a dinitrile.

3. α-Phenylbutyronitrile was not found to condense with itself under the influence of sodium ethylate in ether.

4. The syntheses of the chloride and amide of α-phenylbutyric acid are reported.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

CARBON TETRABROMIDE AS A BROMINATING AGENT[1]

BY W. H. HUNTER AND D. E. EDGAR

RECEIVED JANUARY 2, 1932 PUBLISHED MAY 7, 1932

During the study of certain reactions of carbon tetrabromide and aniline in xylene solution, it was observed that the xylene was brominated. Accordingly, an investigation was started with the point of view of determining the possible use of carbon tetrabromide as a brominating agent. In the case of the majority of compounds studied, bromination with this reagent took place, and when this occurred bromoform was always a by-product. Most of the bromo compounds prepared in this work can be made more easily by other methods, so that, as a rule, the use of carbon tetrabromide does not have any advantages over the commoner methods, but our experiments indicate that there are certain regularities with brominations using carbon tetrabromide that may be very useful, and the most important of these is the preferential side chain bromination of alkylbenzenes.

Experimental Part

Preparation of Carbon Tetrabromide.—The method of Wallach[2] served as a basis for our modified preparation of carbon tetrabromide from acetone and sodium hypobromite. The preparation as described is suitable for the production of large quantities of carbon tetrabromide in good yield. Since bromoform is a by-product in all cases of brominations described here, use was also made of a method similar to Habermann's,[3] involving bromoform and aqueous sodium hypobromite. Although Habermann stated that direct light was necessary, it was found that as good a yield of carbon tetrabromide could be obtained in the complete absence of light.

[1] The work described in this paper constituted part of a thesis submitted to the graduate faculty of the University of Minnesota by Donald E. Edgar in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1927. This paper was prepared by the junior author after the death of Dr. Hunter.—[L. I. SMITH.]

[2] Wallach, *Ann.*, **275**, 149 (1893).

[3] Habermann, *ibid.*, **167**, 174 (1873).

(a) From Acetone.—A four-liter container (fitted with a mechanical agitator) was approximately half-filled with shaved ice. To this was added 2500 cc. of sodium hydroxide solution containing 150 g. of sodium hydroxide to the liter; 200 cc. of bromine was added rapidly with stirring. Then 60 cc. of acetone was added in small portions (5–10 cc.), time being allowed after each addition for the milky precipitate formed (probably bromoform) to be converted into lumps of carbon tetrabromide. After addition of this amount of acetone, 1-cc. portions were added cautiously until the characteristic yellow hypobromite color had been discharged. The crude carbon tetrabromide was separated by filtration and purified by crystallization from alcohol.

(b) From Bromoform.—A sodium hypobromite solution was prepared as in (a) but with only one-fourth of the amounts of materials. This is sufficient to convert 150 g. of bromoform to carbon tetrabromide. All of the bromoform was added at one time and the mixture was shaken or stirred vigorously.

Procedure in Bromination Experiments.—The reactions were carried out by heating carbon tetrabromide with various materials in sealed tubes, in the proportions of 1:1 unless otherwise noted. The temperature, in general, was 150–180°, and the time of heating about eight hours. In practically all cases, separation and purification of resulting products was accomplished by fractional distillation under diminished pressure. Identification of the products was by analysis for bromine, together with physical properties. The method of analysis was that of Stepanoff, as modified by Drogin and Rosanoff,[4] which was found to be rapid and convenient.

TABLE I

RESULTS OF EXPERIMENTS IN WHICH ALIPHATIC COMPOUNDS WERE THE REACTANTS WITH CARBON TETRABROMIDE

Reactants with CBr_4	Product	Yield, %
n-Heptane	Decomposition	..
Acetic acid	Bromoacetic acid	32.4
Propionic acid	α- and β-monobromopropionic acids (mixture)	42.2
Sym.-tetrabromoethane	Pentabromoethane	10.1
	Hexabromoethane	2
Pentabromoethane	Hexabromoethane	Trace

TABLE II

RESULTS WITH AROMATIC COMPOUNDS

Reactants with CBr_4	Product	Yield, %
Benzene	Bromobenzene	67.6
Toluene	Benzyl bromide	76.9
Ethylbenzene	1-Phenyl-1-bromoethane	66.6
Ethylbenzene[a]	1-Phenyl-1,2-dibromoethane	70.3
n-Propylbenzene	1-Phenyl-1-bromopropane	46.7
Cumene	Decomposition	..
m-Xylene	*m*-Xylyl monobromide	67.3
m-Xylene[a]	*m*-Xylylene dibromide	48.4
Durene	Duryl monobromide	33.5
Durene[b]	Addition product, 1:1	100
Naphthalene	α-Bromonaphthalene	74.5

[a] Two moles of carbon tetrabromide to one of reactant. [b] Room temperature in carbon disulfide solution.

[4] Drogin and Rosanoff, THIS JOURNAL, **38,** 711 (1916).

In the study of aromatic hydrocarbons, described above in Table II, several interesting facts were noted. Bromination, by this method, takes place preferentially in the side chain rather than in the ring: the first point of attack being, in these cases, the alpha carbon of the chain. The decomposition of isopropylbenzene, whereas *n*-propylbenzene is brominated, suggests a method of differentiating between normal and iso linkages to the ring.

Duryl Monobromide ($C_{10}H_{13}Br$).—This compound, which has not heretofore been prepared, resulted from the reaction of carbon tetrabromide and durene in the general manner described above and in Table II. Duryl monobromide is a clear, practically colorless liquid boiling at 110–112° under a pressure of 4 mm. It has a not unpleasant odor, somewhat resembling that of benzyl bromide, but is free from lachrymatory action. With alcoholic silver nitrate it gives an immediate precipitate of silver chloride, while monobromodurene, a solid having a melting point of 61°—the only other monobromo derivative of durene—gives no precipitate.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.51. Found: (Stepanoff) Br, 37.78, 37.69; (Carius) Br, 37.88, 37.82; (alc. $AgNO_3$) Br, 37.81, 37.86.

Durene—Carbon Tetrabromide Addition Product ($C_{10}H_{14}\cdot CBr_4$).[5]—Durene and carbon tetrabromide were dissolved in equivalent molecular proportions in an excess of carbon disulfide. The solution was allowed to stand at room temperature until the carbon disulfide had evaporated. The material remaining was in the form of large, well-defined crystals different in form from those of durene or of carbon tetrabromide, m. p. 84–86°. Mixed melting points of this material with either durene or carbon tetrabromide gave a lowering of the melting point.

Anal. Calcd. for $C_{10}H_{14}\cdot CBr_4$: Br, 68.62. Found: Br, 68.29, 68.51.

TABLE III

REACTIONS WITH AROMATIC COMPOUNDS

Reactants with CBr_4	Product	Yield, %
Bromobenzene	*p*-Dibromobenzene	42.5
p-Dibromobenzene	No reaction	..
Benzyl bromide	Benzal bromide	55.3
	Benzal bromide	74.5[d]
Benzyl bromide[a]	Benzotribromide	21.4
Benzal bromide	Benzotribromide	27.2
Phenol[b]	(Aurin)	..
Aniline[c]	(Pararosaniline)	..

Nitrobenzene, *m*-dinitro benzene, and benzoic acid gave no reaction, even on prolonged heating, while hydroquinone was completely decomposed.

[a] Two moles of carbon tetrabromide to one of reactant. [b] One mole of carbon tetrabromide to ten of reactant; refluxed for thirty minutes. [c] One mole of carbon tetrabromide to thirteen of reactant; refluxed for one hour. [d] Temperature, 210°.

Table III records the reactions of various aromatic compounds. It is interesting to note that bromination did not take place with any of the compounds having a meta orienting group already present. Phenol and carbon tetrabromide when heated together at atmospheric pressure gave a bright red material which was not studied further at this time. It was perhaps aurin, since Gomberg and Snow[6] have described the formation of this dye from phenol and carbon tetrachloride. Likewise, in the case of aniline, para-

[5] We wish to express our thanks to Dr. L. I. Smith for his generosity in providing the durene and bromodurene which made possible these experiments.

[6] Gomberg and Snow, THIS JOURNAL, **47**, 198 (1925).

rosaniline was perhaps the product since Hofmann[7] obtained it similarly by the action of carbon tetrachloride.

It will be noted in Table III that benzotribromide was the product of two reactions. This compound is described here for the first time, as far as the writers are aware. A search of the literature revealed only one mention[8] of this compound and that was in a statement to the effect that benzotrichloride (or bromide) is readily hydrolyzed by water or potassium hydroxide to benzoic acid. It was found that several hours of heating with 10% sodium hydroxide was required to bring about hydrolysis of a 3-g. sample.

Benzotribromide ($C_7H_5Br_3$).—Benzotribromide resulted from the reaction of two equivalents of carbon tetrabromide with one of benzyl bromide and also from one equivalent of carbon tetrabromide with one of benzal bromide. Hydrolysis of the product resulted in the formation of benzoic acid.

Benzotribromide is a colorless crystalline material, very soluble in alcohol or ether, less soluble in petroleum ether, insoluble in water: m. p. 56–57°.

Anal. Calcd.: Br, 72.91. Found: Br, 72.76, 72.61 (Stepanoff); 72.85 (alc. $AgNO_3$).

Summary

1. Carbon tetrabromide will react with various organic materials through the exchange of a bromine atom for a hydrogen. Bromoform is always the by-product of such bromination.

2. Carbon tetrabromide brominates selectively the side chains of the benzene hydrocarbons instead of attacking the ring.

3. Duryl monobromide, benzotribromide, and an addition product of durene and carbon tetrabromide are described.

[7] Hofmann, *J. prakt. Chem.*, **77**, 191 (1859); **87**, 226 (1862).

[8] Fry, THIS JOURNAL, **36**, 1043 (1914).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

SUBSTITUTED PHENYLACETONITRILES AND DERIVATIVES. 1-PHENYL-1-CYANOCYCLOPROPANE, ALPHA-PHENYL-GAMMA-HYDROXYBUTYRONITRILE, ALPHA-PHENYL-GAMMA-CHLOROBUTYRONITRILE AND ALPHA-PHENYLCROTONONITRILE[1]

BY EDWIN C. KNOWLES AND JOHN B. CLOKE

RECEIVED JANUARY 2, 1932 PUBLISHED MAY 7, 1932

In the development of a series of investigations on sundry cyclic ketimines, imino esters and heterocyclic nitrogen compounds, supplies of α-alkyl and α-aryl-γ-chlorobutyronitriles and alkyl and aryl substituted cyclopropyl cyanides were required. The present paper describes the preparation of one of the chloro and two of the cyclic compounds.

[1] This paper is from the first part of a thesis presented by Edwin Chandler Knowles in June, 1931, to the Graduate School of the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

The Preparation of 1-Phenyl-1-cyanocyclopropane, $\overline{CH_2CH_2C}(C_6H_5)$-CN.—Two methods have been developed for the preparation of 1-phenyl-1-cyanocyclopropane (I). In the first method one mole of phenylacetonitrile (XIII) in ether was first treated with two moles of sodium amide, and this reaction mixture was then allowed to react with ethylene chlorobromide or dibromide under suitable conditions to give 40–45% yields of (I). This procedure, therefore, constitutes an extension of the work of Bodroux and Taboury[2] on the alkylated phenylacetonitriles to the alkylene derivatives.

The first stage in the formation of (I) by the foregoing method involves the reaction of the sodium amide with (XIII) to give the monosodium salt. In accordance with the views of Rising[3] and others the carbide tautomer of this salt may then be assumed to react with the ethylene chlorobromide to give primarily sodium bromide and α-phenyl-γ-chlorobutyronitrile (XIV).

$$ClCH_2CH_2Br + Na^+{}^-CH(C_6H_5)CN = ClCH_2CH_2CH(C_6H_5)CN + Na^+{}^-Br \quad (1)$$

In the third stage of the reaction, (XIV) may be supposed to react with the excess sodium amide and with the salt of (XIII) to give the tautomeric carbide and nitride salts, and, finally, the carbide salt may be regarded as undergoing a very rapid internal condensation to give (I) and sodium chloride

$$ClCH_2CH_2C^-(Na^+)(C_6H_5)CN = \underline{CH_2CH_2C}(C_6H_5)CN + Na^+Cl^- \quad (2)$$

The mechanism which has been suggested for the latter ring closure is the same as that which has been given in detail for the preparation of cyclopropyl cyanide from γ-chlorobutyronitrile.[4]

That the formation of (I) by Method 1 actually goes through the stages as sketched above seems clear from other considerations. Thus, in the first place, slightly less than one equivalent of ammonia is liberated for each mole of (XIII) which is used, even though twice as much sodium amide is present. In the second place (XIV), whose existence as an intermediate has been postulated in Equation 1, has been found to react with sodium amide to give (I). This reaction, which is formulated in Equation 2, constitutes the second method for the preparation of (I).

α-Phenyl-γ-chlorobutyronitrile.—Compound (XIV) was obtained by the action of thionyl chloride on α-phenyl-γ-hydroxybutyronitrile in pyridine solution

$$HOCH_2CH_2CH(C_6H_5)CN + SOCl_2 = ClCH_2CH_2CH(C_6H_5)CN + SO_2 + HCl \quad (3)$$

[2] Bodroux and Taboury, *Bull. soc. chim.*, **7**, 666 (1910); *Compt. rend.*, **150**, 531, 1241 (1910).

[3] Rising and Zee, THIS JOURNAL, **49**, 541–545 (1927); **50**, 1699–1707 (1928); Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929).

[4] Cloke, Anderson, Lachmann and Smith, *ibid.*, **53**, 2791 (1931).

This procedure was suggested by the work of Darzens[5] on the replacement of hydroxyl in alcohols and hydroxy esters by chlorine.

α-Phenyl-γ-hydroxybutyronitrile.—The hydroxynitrile which was required in Equation 3 was prepared by the action of ethylene chlorohydrin on the sodium salt of (XIII).

$$HOCH_2CH_2Cl + Na^+{}^-CH(C_6H_5)CN = HOCH_2CH_2CH(C_6H_5)CN + Na^+Cl^- \quad (4)$$

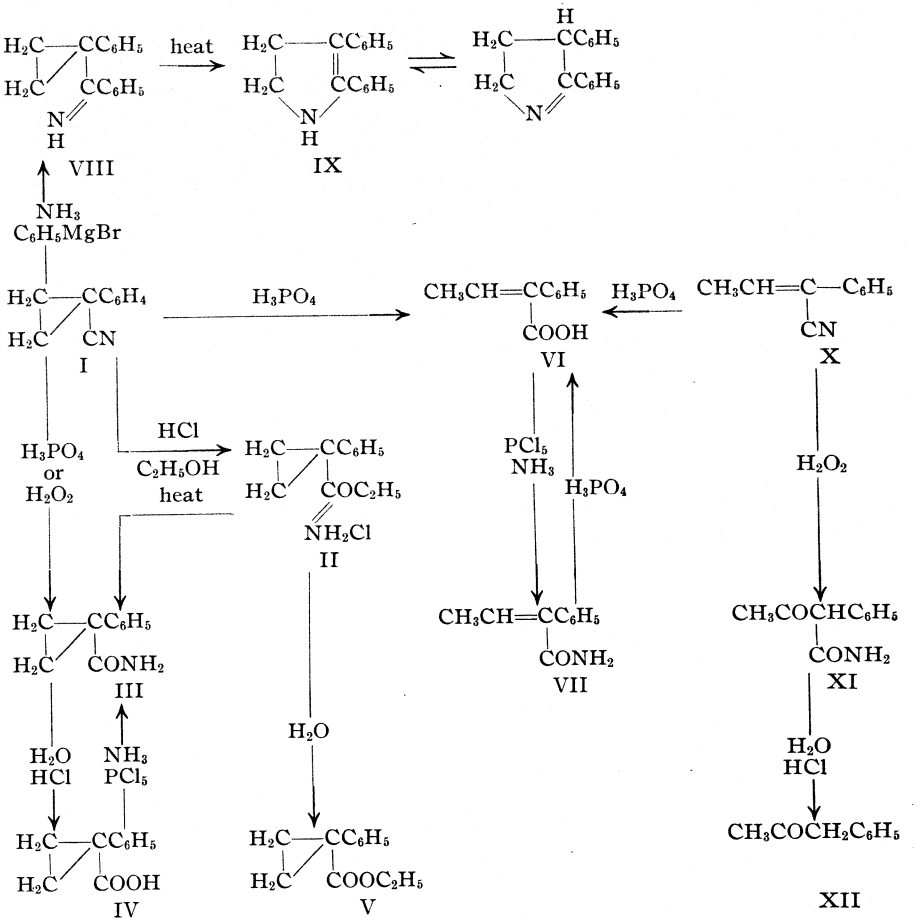
The Structure of the 1-Phenyl-1-cyanocyclopropane.—At one time it appeared likely that our nitrile (I) which was obtained by Method 1 might be one of the geometrical isomers of the isomeric α-phenylcrotononitrile (X), since the amide which was obtained from (I) was found to have the same melting point as that which had been reported by Pfeiffer, Engelhardt and Alfuss[6] for the α-phenylcrotonamide (VII). It seemed possible, therefore, that the isomeric (X) might either have arisen directly from (I) by a ring rupture or from the rearrangement of α-phenylvinylacetonitrile, which might have been the initial product by Method 1. Now, however, several lines of evidence point unquestionably to the cyclopropane structure (I).

In the first place nitrile (I) is different from (X). Thus (I) was saponified by phosphoric acid and also by alkaline hydrogen peroxide to give the amide of 1-phenylcyclopropanecarboxylic acid (III), which was distinct from the amide (VII) which can be prepared from the α-phenylcrotonic acid (VI) by the action of phosphorus pentachloride and ammonia. It is true that the amides melted at practically the same temperature, but they had distinct crystalline structures and gave a decidedly lower mixed melting point. Moreover, the real (X) was difficultly saponified by hydrogen peroxide and dilute alkali to give α-phenylacetoacetamide (XI), which was recognized from its analysis and from the fact that it gave methyl benzyl ketone (XII) on hydrolysis. It is also of interest to note that (I) reacted with hydrogen chloride and ethanol to give the imino ester hydrochloride (II), which in turn gave the amide (III) on heating, whereas the isomeric nitrile (X) failed to react under these conditions. Finally (I) and (X) gave characteristic ketimines.

The saponification of (I) with hot phosphoric acid gave not only the amide (III) but also the acid (VI), which originated as the result of a ring rupture. The acid, indeed, was the main product. Cyanocyclopropane itself under the same conditions gave cyclopropanecarboxylic acid. The corresponding acid (IV) was obtained from the amide (III) by saponification with boiling dilute hydrochloric acid. That no ring rupture had occurred in this reaction was established by the reconversion of the acid (IV) into the amide (III) by means of phosphorus pentachloride and ammonia.

[5] Darzens, *Compt. rend.*, **152**, 1314, 1601 (1911).

[6] Pfeiffer, Engelhardt and Alfuss, *Ann.*, **467**, 189 (1928).



That the nitrile (I) could not be the α-phenylvinylacetonitrile was shown, on the one hand, by its failure to react significantly either with bromine in carbon tetrachloride or with alkaline potassium permanganate solution, and, on the other hand, by its saponification to the acid (IV) which failed to rearrange to (VI) when it was treated with a base. Independent work of Gilman and Harris[7] and by the writers on the vinylphenylacetic acid has established this point.

That the nitrile (I) is not the geometric isomer of (X) and that it actually has the cyclic structure (I) was finally established beyond question by the complete analogy which exists between the behavior of phenylcyclopropyl ketimine, $CH_2CH_2CHC(=NH)C_6H_5$,[8] and the 1-phenylcyclopropyl phenyl ketimine (VIII), which has been prepared from (I) by the Grignard

[7] Gilman and Harris, THIS JOURNAL, **53**, 3544–3545 (1931).

[8] Cloke, *ibid.*, **51**, 1174 (1929); Doctorate Dissertation, University of Chicago.

reaction. Thus, the two ketimine hydrochlorides react with water at almost the same rate, and, second, and this is of most significance, both ketimines rearrange to give the corresponding pyrrolines, *e. g.*, (IX). An account of this work will appear later. Finally, it may also be noted that the structure (I) would likewise be indicated from the second method of synthesis, namely, from (XIV), since the γ-chlorobutyronitrile gives cyanocyclopropane under the same conditions.

α-Phenylcrotononitrile.—The nitrile (X), which was required in connection with the study of the structure of (I), was obtained in a 36% yield by the condensation of acetaldehyde with benzyl cyanide in the presence of sodium ethylate at 0°

$$CH_3CHO + H_2C(C_6H_5)CN = CH_3CH{=}C(C_6H_5)CN + H_2O \qquad (5)$$

Pfeiffer, Engelhardt and Alfuss, who obtained the nitrile by another method, assigned to it the *cis* configuration, namely, $\begin{matrix} C_6H_5{-}C{-}CN \\ \| \\ H{-}C{-}CH_3 \end{matrix}$, in view of the fact that the compound is very slowly esterified. Our failure to transform it into the ethyl imino ester hydrochloride constitutes evidence of the same type for this structure.

Experimental Part

Preparation of 1-Phenyl-1-cyanocyclopropane by Method 1.—A one-liter, three-necked, round-bottomed flask was provided with a 500-cc. dropping funnel, a mechanical stirrer, which operated through a mercury seal, and a reflux condenser. The open ends of the funnel and condenser were provided with drying tubes. In the later runs a suction arrangement, which is illustrated in Fig. 1, was also attached to the apparatus, whereby the contents of the flask could be transferred to the funnel without the necessity of their exposure to the moist air of the laboratory. Finally the apparatus was thoroughly dried with a current of warm dry air.

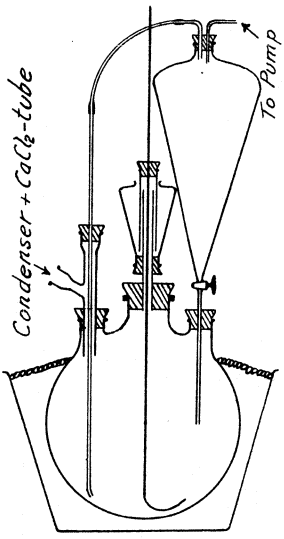


Fig. 1.

A weight of 75 g. (1.92 moles) of Kahlbaum's sodium amide was halved and each part was converted into a flocculent condition under about 200 cc. of anhydrous ether by a process of elutriation. Throughout this alternate process of grinding and decantation care was taken to avoid as much as possible the direct exposure of the sodamide to moist air. In passing it may be added that no explosive decompositions have occurred with us since we have ground the sodium amide under ether, although several took place before. The finely ground compound was at once transferred to the reaction flask with 400–450 cc. of the ether under which it had been pulverized. One mole (117 g.) of phenylacetonitrile[9] was then added to the well-stirred sodium amide suspension from the dropping funnel with sufficient rapidity to give a vigorous refluxing of the ether. As soon as all of the nitrile

[9] Adams and Thal, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 9.

had been added and the vigor of the reaction began to abate, the mixture was refluxed gently on a water-bath for four to five hours, whereby about 0.9 mole of the monosodium salt was formed upon the basis of the quantity of ammonia evolved. Longer periods of refluxing did not serve to increase this amount of salt. Furthermore, no noticeably increased yields of the desired nitrile were obtained when the reaction was carried out in an atmosphere of nitrogen, although the color of the reaction mixture was lighter in this case.

At the end of this first stage in the preparation the yellow to dark red reaction mixture was cooled and transferred, preferably by means of the suction arrangement, to the 500-cc. dropping funnel. A weight of 130 g. (0.9 mole) of redistilled Eastman Kodak Co. ethylene chlorobromide[10] in twice its volume of anhydrous ether was then poured into the flask, which at this stage was cooled in an ice–salt bath to −15°. The stirrer was started, and as soon as the solution was thoroughly cold, the sodium salt mixture in the funnel was added to the chlorobromide solution at such a rate that scarcely any refluxing of the ether could be detected.[11] Following the addition of the salt mixture, which required about two hours, the stirring was continued during the next seven hours, while the temperature of the bath was allowed to rise to that of the room. At this stage the temperature of the bath was raised to the point where droplets of ether began to collect in the condenser, where it was held for an hour, and finally it was raised sufficiently to give a gentle refluxing, which was maintained for two hours while the stirring was continued. At the end of this period the evolution of ammonia had completely ceased.

At the conclusion of the foregoing operation enough water was added to the mixture in the flask to dissolve the solid material. The ether layer was then separated and dried over anhydrous sodium sulfate for ten hours. Distillation of the dry filtered ether solution under diminished pressure on the water-bath gave 15 g. of a fraction which boiled from 81–83° at 1 mm.; this was mainly benzyl cyanide. The continuation of the distillation under the same pressure but with direct heating gave 91.5 g. of the main product, which boiled from 110–113°, and 18–20 g. of a tarry residue which was not examined. Redistillation of the main fraction through a modified Claisen–Vigreux flask with a 1.8 × 30 cm. column gave 60–64 g. of distillate which boiled from 98–100° at less than 1 mm.; this corresponds to a 44% yield upon the basis of the benzyl cyanide used. The freshly distilled product was a colorless oil with a slightly aromatic odor.[12] This liquid boiled from 250–253° at 751 mm. with little decomposition. It possessed a density, d_4^{20}, of 1.0156 and a refractive index, n_D^{20}, of 1.3676, which correspond to a molecular refractivity, $MR_D^{20}(n^2)$ of 43.24 as compared with the calculated value of 43.10.

Anal. Subs., 8.44 mg., 9.78 mg.: N_2 (corr.), 0.657 cc.; N_2 (corr.), 0.763 cc. Calcd. for $C_{10}H_9N$: N, 9.79. Found: N, 9.72, 9.75.

Preparation of 1-Phenyl-1-cyanocyclopropane by Method 2.—The 1-phenyl-1-cyanocyclopropane was also prepared by the action of 8.1 g. of sodium amide on 31.5 g. of α-phenyl-γ-chlorobutyronitrile in 200–250 cc. of liquid ammonia by a process similar

[10] In one run in which 42 g. of sodium amide, 58 g. of benzyl cyanide and 92 g. of ethylene dibromide were employed, 12 g. of product was obtained. This yield could doubtless be improved.

[11] In one experiment in which the ethylene chlorobromide was added to the sodium salt mixture, the result was practically as good as in the procedure described, although we believe the latter method is safer.

[12] The last traces of benzyl cyanide may be removed from the final product by its condensation with benzaldehyde in accordance with the process of Meyer and Frost, *Ann.*, **250**, 157 (1889).

to that of Cloke, Anderson, Lachmann and Smith. A 73% yield (18.5 g.) of product was obtained.

α-Phenyl-γ-chlorobutyronitrile.—In the first run 77 g. (0.48 mole) of α-phenyl-γ-hydroxybutyronitrile from the following preparation and 38 g. (0.48 mole) of pyridine were placed in a 500-cc. three-necked flask, which was equipped with a reflux condenser, a mechanical stirrer and a dropping funnel. To this solution, which was cooled by the immersion of the flask in an ice-bath, 57 g. (0.48 mole) of thionyl chloride was slowly added from the dropping funnel with constant stirring. At the end of this addition the mixture was heated in a water-bath at 80–85° for thirty minutes. Water was then added and the heating was continued for about two hours. At this stage the mixture was cooled and extracted with ether. The ether extract in turn was extracted with dilute acid, which was followed by water, 10% sodium carbonate solution and finally by several portions of water. The ether extract was then dried over calcium chloride and distilled in a Claisen flask. The fraction which boiled from 97–135 at 3–4 mm. and which weighed 50 g. was redistilled in a Claisen–Vigreux flask. Two fractions were collected: the first (15 g.) was collected between 98–125°; and the second (31.5 g.), which was taken for analysis, boiled from 127–129° at 3–4 mm.; d_4^{20} 1.1251; n_D^{20} 1.5327; mol. ref. calcd., 49.42; found (n^2 formula), 49.51. The product was an oily liquid with a pleasant aromatic odor and was tinged slightly yellow, doubtless on account of the presence of a trace of impurity.

Anal. Subs., 11.12 mg.: N_2 (S. T. P. corr.), 0.699 cc. Calcd. for $C_{10}H_{10}NCl$: N, 7.80. Found: N, 7.88.

In a second run the α-phenyl-γ-hydroxybutyronitrile was mixed with a small excess of pyridine in the dropping funnel and added to the thionyl chloride which was contained in the flask. This procedure, however, reduced the yield of the desired product to 13 g., which was less than half of the amount which was obtained in the first run.

α-Phenyl-γ-hydroxybutyronitrile.—A weight of 120 g. (1.03 mole) of benzyl cyanide was allowed to react with 40 g. of sodium amide in the presence of 200 cc. of anhydrous ether. Enough ether was then added to bring the total volume to about 700 cc., and the mixture was refluxed gently on the water-bath for four hours with constant stirring. Here the water-bath was replaced by an ice-bath and, as soon as the mixture was well chilled, 85 g. (1.06 mole) of ethylene chlorohydrin was added slowly and with constant stirring over a period of about two hours. The ice-bath was then removed and the stirring was continued at room temperature for five hours, when the amount of precipitate seemed to have become constant. Enough water was then added to dissolve all of the solid, when the ether layer was separated and dried over anhydrous sodium sulfate. Three fractions were obtained: the first (34 g.) was mainly benzyl cyanide; the second (64 g. of b. p. 160–168° at 2–3 mm.) was primarily the desired nitrile; while the residue was not examined. Redistillation of the middle fraction gave a product of b. p. 146–149° at 1.5–2.0 mm., and this was taken for analysis. The freshly distilled compound was a nearly colorless and very viscous oily substance. A sample which had been allowed to stand for two years was found to have changed into a pasty wax-like substance. The density of the freshly distilled compound, d_4^{20}, was 1.065; and its index of refraction, n_D^{20}, was 1.5411.

Anal. Subs., 0.3125 g.: CO_2, 0.8500; H_2O, 0.1976. Subs., 19.91 mg., 17.18 mg.: N_2 (S. T. P. corr.) 1.394, 1.183 cc. Calcd. for $C_{10}H_{11}ON$: C, 74.49; H, 6.88; N, 8.69. Found: C, 74.18; H, 7.08; N, 8.76, 8.61.

Mol. wt. Subs., 0.2725; ethyl acetate, 17.38 g.; boiling point rise, 0.265°. Calcd. for $C_{10}H_{11}ON$: mol. wt., 161.09. Found: 158.7.

In a second run, in which the sodium salt of benzyl cyanide in ether was added to

a 25% excess of ethylene chlorohydrin, the yield of nitrile was somewhat smaller than by the above process. In a third run, which was similar to the first, but in which the temperature of the reaction flask was lowered to −15° during the addition of the chlorohydrin, a larger quantity of benzyl cyanide was recovered, but the yield of the hydroxy compound was not materially increased.

1-Phenyl-2-methyl-1-cyanocyclopropane, $\overline{CH_2CH(CH_3)C(C_6H_5)CN}$.—Two moles (80 g.) of finely pulverized sodium amide in about 200 cc. of anhydrous ether was treated with 0.9 mole (105 g.) of benzyl cyanide as in the preparation of the 1-phenyl-1-cyanocyclopropane. To this mixture, which was cooled in an ice-bath, 0.9 mole (180 g.) of propylene dibromide was added. A very vigorous reaction ensued. The completion of the reaction gave 26 g. of a colorless oil with a slightly ethereal odor of b. p. 257–260° at 761 mm.; d_4^{20} 1.0115; n_D^{20} 1.5316.

Anal. Subs., 13.880 mg.: N_2 (corr.), 0.982 cc. Calcd. for $C_{11}H_{11}N$: N, 8.91. Found: N, 8.84.

The Amide of 1-Phenylcyclopropanecarboxylic Acid.—By the general process of Radziszewiski[13] the 1-phenyl-1-cyanocyclopropane was converted into the amide by the first method. The fine, glistening, needle-shaped crystals melted at 81–83° when heated rapidly and at 95–96° when heated slowly. The product which had been dried at 50–60° under diminished pressure for several hours softened at 96° and melted completely at 97–98° (uncorr.) or at 100–101° (corr.). From these results it was assumed that the air-dried product was hydrated. No evidence was secured which suggested the ring rupture of the amide below 250°.

Anal. Subs., 11.69 mg.: N_2 (corr.), 0.803 cc. Calcd. for $C_{10}H_{11}ON$: N, 8.69. Found: N, 8.59.

Mol. wt. (Rast) Subs., 2.59 mg.; camphor, 24.52 mg.; freezing point lowering, 26.13°. Calcd. for $C_{10}H_{11}ON$: mol. wt. 160.1. Found: 161.7.

The foregoing amide was also obtained in a second way by the heating of ethyl imino-1-phenylcyclopropane-carboxylate hydrochloride to approximately 110°.

By a third method 2 g. of nitrile was heated at 140° with 30 g. of "100%" phosphoric acid (70 g. of 85% H_3PO_4 + 30 g. of P_2O_5) for three and one-half hours by the Berger–Olivier[14] method. The cooled acid solution was poured onto cracked ice, the aqueous solution was extracted with ether, and the ether was finally extracted twice with sodium hydroxide solution and once with water. Evaporation of the dried and filtered ether extract gave the amide of m. p. 100–101° (corr.) after two recrystallizations.

The Rupture of the Ring in the Formation of α-Phenyl-crotonic Acid from 1-Phenyl-1-cyanocyclopropane.—The acidification of the sodium hydroxide solution from the preceding reaction gave the acid of m. p. 135.5–137°[15] after two recrystallizations. A mixed melting point determination with the acid which was obtained from α-phenylcrotononitrile by the same method gave no depression.

The Action of Hot Phosphoric Acid on Cyanocyclopropane.—The unsubstituted cyclopropyl cyanide by the foregoing saponification method gave the cyclopropanecarboxylic acid, which gave an anilide of m. p. 110–111° by the method of Autenrieth and Pretzell.[16]

---

[13] Radziszewiski, *Ber.*, **18,** 355 (1885); McMaster and Langreck, THIS JOURNAL, **39,** 103 (1917).

[14] Berger and Olivier, *Rec. trav. chim.*, **46,** 600–604 (1927).

[15] Dimroth and Feuchter, *Ber.*, **36,** 2238 (1903).

[16] Autenrieth and Pretzell, *ibid.*, **38,** 2548 (1905).

1-Phenylcyclopropanecarboxylic Acid.—By the saponification of the amide of the 1-phenylcyclopropanecarboxylic acid with boiling concentrated hydrochloric acid, the corresponding acid was obtained. The dry needle-like crystals melted at 86–87° (uncorr.). That no ring rupture had occurred in this reaction was demonstrated by the reconversion of the acid into the original amide by means of phosphorus pentachloride and ammonia.

α-Phenylcrotononitrile.—A solution of 160 g. (1.36 moles) of benzyl cyanide, 250 g. of absolute alcohol and 88 g. (2 moles) of acetaldehyde, which was prepared by the depolymerization of paraldehyde, was chilled to −5° and treated gradually with 15 cc. of freshly prepared 20% sodium ethylate so that the temperature did not rise above 0°. The yellowish-red solution was then placed in a refrigerator for a day, when an additional 10-g. portion of acetaldehyde was added, which was followed by a further sixteen-hour stand in the ice box. Three hundred cc. of water was then added to the mixture, which was well shaken, and the oily layer was separated and washed with another 300-cc. portion of water. The fractionation of the dried oil gave finally 70 g. (35.8% yield) of the nitrile, b. p. 100–103° at 1 mm. or less. The freshly distilled oily compound was colorless with a somewhat musty unpleasant odor, but it turned slightly yellowish on standing. It boiled at 244–246° at 751 mm. with a marked discolorization: d_4^{20} 1.013, n_D^{20} 1.5555, MR_D^{20} 45.41; calcd., 45.10.

Anal. Subs., 10.844 mg.: N_2 (corr.), 0.841 cc. Calcd. for $C_{10}H_9N$: N, 9.79. Found: N, 9.70.

Excessively alkaline solutions were found to be disadvantageous for the foregoing condensation, since they led to the formation of large amounts of resinous tarry materials, which was also the case when the condensation of ethylidene chloride and benzyl cyanide with sodium amide was attempted. Moreover, the use of such condensing agents as acetic acid–acetic anhydride, alcoholic ammonia and piperidine was unsuccessful.

α-Phenylacetoacetamide.—With the expectation of obtaining α-phenylcrotonamide, the α-phenylcrotononitrile was subjected to the action of alkaline hydrogen peroxide. The pure white solid which was formed was insoluble in cold water, fairly soluble in ether, alcohol and acetone and readily soluble in dioxane. The dried sample melted at 177–178°. Solutions of the compound in acetone and dioxane did not appear to be changed by long exposure to an ultraviolet light.

Anal. Subs., 10.478 mg., 11.838 mg.: N_2 (corr.), 0.642 cc.; N_2 (corr.) 0.749 cc. Calcd. for $C_{10}H_{11}NO_2$: N, 7.91. Found: N, 7.66, 7.91.

Mol. wt. Subs., 1.108 mg., 0.871 mg.; camphor, 10.576 mg., 10.099 mg.; temperature lowering, 23.73, 19.68°. Calcd. for $C_{10}H_{11}NO_2$: mol. wt. 177.09. Found: 176.6, 175.3.

Methyl Benzyl Ketone from the α-Phenylacetoacetamide.—In order to establish the identity of the acetoacetamide it was saponified with boiling concentrated hydrochloric acid. The semicarbazone into which the resulting ketone was converted melted at 188.5–189.5°, whereas the recorded value[17] for this derivative of the methyl benzyl ketone is 188–189°, although higher values have been reported.

α-Phenylcrotonic Acid from the Nitrile.—The saponification of α-phenylcrotononitrile by the hot phosphoric acid method gave the acid, m. p. 136–137°.

α-Phenylcrotonic Acid from Phenylvinylacetic Acid.—In order to show that phenylvinylacetic acid would rearrange to give the isomeric crotonic acid, the following program was followed. First phenylvinylcarbinol was prepared from 48.5 g. of magnesium, 314 g. of bromobenzene, 580 cc. of anhydrous ether and 92 g. of freshly prepared acrolein

[17] Wolff, *Ann.*, **325**, 146 (1902).

by a modification of the process of Klages and Klenk.[18] The carbinol was then converted into 1-phenyl-1-chloropropene-2 by the saturation of its ether solution with dry hydrogen chloride,[18,19] which gave, with certain modifications, 215 g. of the chloride. Finally a Grignard reagent was prepared by a special procedure from 18 g. of magnesium, 100 cc. of ether and 30 g. of the chloride in five volumes of ether. This reagent was then carbonated as usual, and the salt was decomposed in a cold acid solution. Evaporation of the ether extract of the acid under diminished pressure left 7–8 g. of a brownish oil, which crystallized after several hours in an ice–salt bath and which was presumably the phenylvinylacetic acid. This was then treated with 15 cc. of 10% sodium hydroxide solution, and from this the α-phenylcrotonic acid was prepared. The acid was characterized by its melting point and by its transformation into the *p*-nitrobenzyl ester, m. p. 80–81°, and the amide.

Summary

1. 1-Phenyl-1-cyanocyclopropane can be obtained in 40–45% yields by the condensation of ethylene chlorobromide with phenylacetonitrile by means of sodium amide. The same cyclic compound has been prepared in 73% yield by the action of sodium amide on α-phenyl-γ-chlorobutyronitrile. Several derivatives and reactions of the cyclic nitrile have been described in connection with a critical proof of its structure.

2. The preparation of 1-phenyl-2-methyl-1-cyanocyclopropane has been described.

3. α-Phenyl-γ-chlorobutyronitrile can be obtained by the action of thionyl chloride on α-phenyl-γ-hydroxybutyronitrile in pyridine solution.

4. α-Phenyl-γ-hydroxybutyronitrile has been obtained in a 40% yield by the action of ethylene chlorohydrin on the sodium salt of phenylacetonitrile.

5. α-Phenylcrotononitrile has been prepared in a 36% yield by the condensation of acetaldehyde with benzyl cyanide.

6. The action of alkaline hydrogen peroxide solution on α-phenylcrotononitrile led to the formation of α-phenylacetoacetamide.

7. The preparation of α-phenylcrotonic acid from the α-phenylcrotononitrile, the 1-phenyl-1-cyanocyclopropane and by a Grignard synthesis has been described.

Other papers will follow on the extension of the work described in this paper to other analogous compounds and their derivatives.

TROY, N. Y.

[18] Klages and Klenk, *Ber.*, **39**, 2552 (1906).

[19] Klages, *ibid.*, **35**, 2650 (1902).

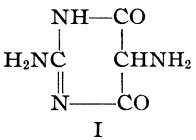
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXXVII.[1] THE STRUCTURE OF CONVICINE[2]

BY HARRY J. FISHER AND TREAT B. JOHNSON

RECEIVED JANUARY 5, 1932 PUBLISHED MAY 7, 1932

The fact that the nucleic acids on hydrolysis yield purine and pyrimidine nucleosides lends great interest to the occurrence in nature of simple pyrimidine glucosides. The only known compounds of this type are the two substances vicine and convicine, isolated by Ritthausen[3] from vetch some sixty years ago.



I

After various investigations by Ritthausen and others[4] it was finally established by Levene[5] that vicine was a glucoside of 2,5-diamino-4,6-dioxypyrimidine I, with the sugar probably attached to the nitrogen of the pyrimidine ring. As Hérissey and Cheymol[6] have recently shown that vicine is hydrolyzed by emulsin, it must be classed as a β-glucoside.

Convicine, which occurs with vicine in vetch, has not, previous to the present study, been isolated by any other investigator than Ritthausen. He showed that it possessed the empirical formula $C_{10}H_{15}N_3O_8 \cdot H_2O$, was distinguished from vicine by not being readily soluble in dilute acids, and on hydrolysis yielded alloxantin and ammonia and a mother liquor which was strongly dextrorotatory and "reacted like sugar solutions to known sugar reagents." Schulze and Trier[4] in 1910 proposed a formula corresponding to alloxantin diglucoside plus two molecules of ammonia attached in some unknown manner. Johnson[4] later pointed out that the formula $C_{10}H_{15}N_3O_8$ corresponded exactly to that of either an aminoglucoside of dialuric acid or a glucoside of uramil.

[1] A report of this research was presented at the Organic Chemistry Symposium held in the Sterling Chemistry Laboratory of Yale University, New Haven, Connecticut, on December 28, 29 and 30, 1931.

[2] This paper is from a portion of a dissertation presented by Harry Johnstone Fisher to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[3] Ritthausen and Kreusler, *J. prakt. Chem.*, **2**, 333 (1870); Ritthausen, "Die Eiweisskörper der Getreidearten," Bonn, 1872, pp. 168–169; *J. prakt. Chem.*, **7**, 374 (1873); *Ber.*, **9**, 301 (1876); *J. prakt. Chem.*, **24**, 202 (1881); *ibid.*, **29**, 359 (1884); Schulze, *Z. physiol. Chem.*, **15**, 140 (1891); *Ber.*, **22**, 1827 (1891); *Z. physiol. Chem.*, **17**, 193 (1893); Ritthausen, *Ber.*, **29**, 894, 2108 (1896); von Lippmann, *ibid.*, **29**, 2653 (1896); Ritthausen, *J. prakt. Chem.*, **59**, 480, 482 (1899); Ritthausen and Preuss, *ibid.*, **59**, 487 (1899); Winterstein, *Z. physiol. Chem.*, **105**, 258 (1919).

[4] Schulze and Trier, *Z. physiol. Chem.*, **70**, 150 (1910–11); Johnson, THIS JOURNAL, **36**, 337 (1914); Johnson and Johns, *ibid.*, **36**, 545 (1914); Fischer, *Ber.*, **47**, 2611 (1914).

[5] Levene, *J. Biol. Chem.*, **18**, 305 (1914); Levene and Senior, *ibid.*, **25**, 607 (1916).

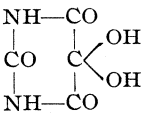
[6] Hérissey and Cheymol, *Compt. rend.*, **191**, 387 (1930); *Bull. soc. chim. biol.*, **13**, 29 (1931).

In an attempt to settle the question of the structure of convicine, the present authors have prepared a sample of this compound from broad beans (*vicia faba*), and have studied its products of hydrolysis and its behavior toward certain reagents.

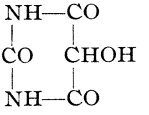
About nine grams of convicine and a small amount of vicine were isolated from the beans. Our convicine was obtained in the form of perfectly colorless glistening, thin flat plates, decomposing without melting at 287°, and analyzing for the formula $C_{10}H_{15}N_3O_8 \cdot H_2O$ found by Ritthausen. It gave a positive murexide test, and a positive Molisch test for carbohydrate. The Wheeler–Johnson test[7] and the color test with ammonia and phosphotungstic acid proposed by Johnson and Johns[8] as a test for the presence of a free amino group in the 5-positions of the pyrimidine cycle, were both negative. Diazobenzene sulfonic acid gave a deep orange-red color with both convicine and vicine. This red color was not found by Johnson and Clapp[9] to be given by pyrimidines which were substituted in the 3-position of the ring. The reaction of convicine with nitrous acid in the Van Slyke apparatus indicated the presence of a free amino group.

The convicine on hydrolysis with sulfuric acid yielded alloxantin (equal to 21.82% of the sample) and one molecule of ammonia. The presence of dextrose in the hydrolysis product was indicated by the formation of glucosazone. Tests for ketoses and pentoses were negative.

If convicine is a monoglucoside, the formula of the nitrogenous base must be $C_4H_5N_3O_3$. The base cannot be alloxantin itself, but must yield alloxantin and ammonia on acid hydrolysis. It is well known[10] that alloxantin in water solution is largely dissociated into alloxan II and dialuric acid III. Any base of the formula $C_4H_5N_3O_3$ which would readily lose one nitrogen atom as ammonia to give either alloxan or dialuric acid would satisfy the structural requirements of the convicine base, as, since there is an oxidation–reduction equilibrium between alloxan and dialuric acid, and since alloxantin is more insoluble than either of these compounds, if either alloxan or dialuric acid were formed by acid hydrolysis of convicine, alloxantin would crystallize from the solution.



II



III

[7] Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).

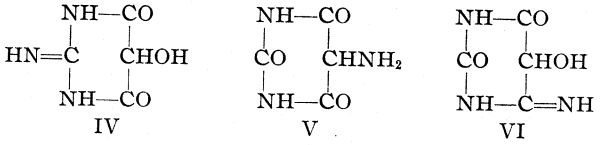
[8] Johnson and Johns, THIS JOURNAL, **36**, 972 (1914).

[9] Johnson and Clapp, *J. Biol. Chem.*, **5**, 163 (1908–9).

[10] Biilmann and Bentzon, *Ber.*, **51**, 522 (1918); Biilmann and Lund, *Ann. chim.*, **19**, 137 (1923); Biilmann and Mygind, *Bull. soc. chim.*, **47**, 532 (1930).

Derivatives of alloxan are excluded from consideration by the fact that they would contain one too many oxygen atoms.

Three possible derivatives of dialuric acid suggest themselves:



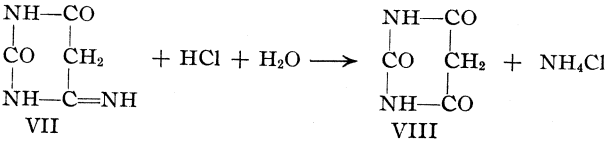
IV V VI

Formula IV is that of 2-iminodialuric acid, V is uramil and VI is 4-iminodialuric acid.

Levene[5] showed that divicine I was oxidized by potassium chlorate and hydrochloric acid with rupture of the pyrimidine ring to yield guanidine. We oxidized some of our convicine in the same manner, and from the reaction product urea was isolated, but no guanidine. This indicates that the convicine base does not contain a 2-imino group, and consequently does not possess the structure IV. There is further no evidence in the literature that a 2-imino group is split off from pyrimidines by dilute acids as ammonia.

If the convicine base possessed the structure of uramil, the 5-amino group should condense with cyanic acid to form a pseudouric acid derivative. Baeyer[11] showed long ago that this reaction did take place with uramil, and Levene[5] in like manner prepared 2-iminopseudouric acid from divicine. We found it impossible to cause any reaction to take place between convicine and potassium cyanate. From this positive evidence, and for the negative reason that there is no evidence in the literature that a 5-amino group is easily lost from a pyrimidine,[12] we believe that the convicine base cannot be uramil, V.

For the third possibility for the structure of the convicine base, that of 4-iminodialuric acid VI, there is strong evidence. While this compound has never been synthesized, its reduced form VII has been prepared by Traube[13] and by Conrad.[14] It is very significant that Conrad found that VII on warming with dilute acids was converted quantitatively to barbituric acid VIII and ammonia



VII VIII

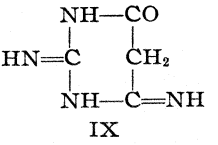
[11] Baeyer, *Ann.*, **127**, 3 (1863).

[12] The statement of Beilstein [3d ed., Ergänzungsband I, p. 767] that 1,3-dimethyluramil is converted into ammonia and tetramethylalloxantin on boiling with hydrochloric acid is evidently due to a misreading of a paper by Fischer and Ach, *Ber.*, **28**, 2475 (1895).

[13] Traube, *Ber.*, **33**, 1381, 3043 (1900).

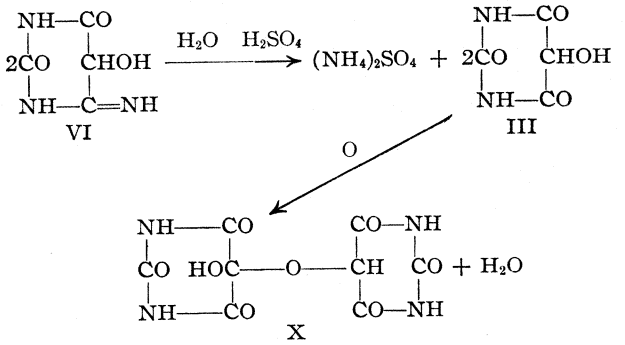
[14] Conrad, *Ann.*, **340**, 310 (1905).

Of particular interest in connection with the relative stability of amino groups in the 2- and 4-positions of the pyrimidine cycle is Conrad's finding that the compound IX was hydrolyzed by dilute acids to 2-iminobarbituric acid and ammonia.



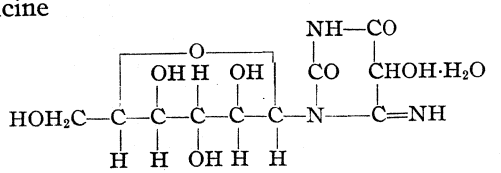
IX

If the imino group in position 4 is so unstable in the barbituric acid derivatives, it is not to be anticipated that it would be any more stable in a dialuric acid derivative such as VI. The quantitative formation of one molecule of ammonia on hydrolysis of convicine with acids, and the presence of alloxantin in the hydrolysis product, are then very simply explained as being due to the hydrolysis of VI to dialuric acid III, which is readily oxidized to alloxantin X



For these reasons the authors believe that the properties of convicine can best be explained by assigning to the pyrimidine nucleus in convicine the structure VI. While the position of attachment of the sugar to this pyrimidine is in doubt, from analogy with vicine and the nucleosides of nucleic acid, and because the Wheeler–Johnson test is negative, the attachment of the sugar to a nitrogen of the pyrimidine ring seems most probable. It is true that convicine is not so highly resistant to acid hydrolysis as are the natural pyrimidine ribosides, which are nitrogen-linked, but the resistance to hydrolysis of the latter is apparently associated with the presence of a 4,5-double bond, and disappears on reduction of this double bond.

The following structure is therefore proposed for the naturally occurring glucoside convicine



Work is now in progress in this Laboratory on methods of synthesizing both vicine and convicine.

The authors wish to express their thanks to Doctors Bailey and Vickery of the Connecticut Agricultural Experiment Station for extending the facilities of their laboratories for part of this investigation, and to Professor W. E. Ford of the Department of Mineralogy, Yale University, for the crystallographic examination of alloxantin.

Experimental Part

The Isolation of Convicine.—Five kilograms of finely powdered broad beans was mixed with 10 liters of 3% sulfuric acid and allowed to stand overnight. The next day the mixture was neutralized with warm 20% barium hydroxide solution and made into a thick paste with filter paper clippings. This paste was squeezed under a hydraulic press, the turbid filtrate made barely acid with sulfuric acid and filtered again on a Buchner funnel through paper pulp. The clear yellow filtrate was treated with an excess of a 10% solution of mercuric sulfate in dilute sulfuric acid, and made alkaline with barium hydroxide solution. The heavy precipitate which came down was allowed to settle, and most of the supernatant liquid was siphoned off. The precipitate was separated from the balance of the liquid and washed with water in a centrifuge. It was then suspended in water with some barium carbonate and the mixture saturated with hydrogen sulfide. The mercuric sulfide was filtered off, and the filtrate concentrated at atmospheric pressure to a volume of 400 cc. The dark red solution was cooled, made just acid to litmus with sulfuric acid, and mixed with 1600 cc. of 95% alcohol. The precipitate which came down was filtered off and the light yellow filtrate was further concentrated *in vacuo* to incipient crystallization. The residue was transferred to a crystallizing dish and placed in a desiccator over sulfuric acid. On standing overnight it usually solidified. It was treated with a little water and the nearly white convicine filtered off. Recrystallization from about 100 parts of boiling water with the addition of a little norite yielded glistening, perfectly white leaflets, decomposing without melting at 287°.

Re-concentration of the mother liquor yielded further amounts of less pure convicine; total yield from 5 kg. of broad beans, 2.32–2.35 g. of crude convicine.

For analysis, the convicine was crystallized four times from boiling water and dried to constant weight at 100°.

Anal. Calcd. for $C_{10}H_{15}N_3O_8 \cdot H_2O$: C, 37.14; H, 5.27; N, 13.01. Found: C, 38.20; H, 5.37; N, 13.08.

Amino nitrogen determinations were run in the micro Van Slyke apparatus on samples of convicine dissolved in half-normal sodium hydroxide: convicine, 0.0100 g., 0.0100 g.: N_2, 0.83, 0.89 cc. at temperature, 30°. Amino N found: 4.5, 4.8.

Convicine is soluble to the extent of about one per cent. in boiling water. It is readily soluble in normal sodium hydroxide and insoluble in chloroform and glacial acetic acid. Its cold saturated aqueous solution does not give a precipitate with potassium mercuric iodide, aqueous iodine–potassium iodide or saturated mercuric chloride, but does give a white precipitate with acid mercuric nitrate solution. Its aqueous solution boiled for two minutes with Fehling's solution shows no copper reduction.

A small amount of vicine was isolated by fractional crystallization of the material obtained by concentration of the mother liquor of the first crop of convicine. It was identified by its melting point (241–242°)[15] and by analysis.

Anal. Calcd. for $C_{10}H_{16}N_4O_7 \cdot H_2O$: N, 17.39. Found: N, 17.72.

Hydrolysis with Sulfuric Acid.—2.000 g. of well-crystallized convicine and 40 cc. of

[15] Levene found 242°; Winterstein, 239–242°.

six normal sulfuric acid were heated for six minutes in a boiling water-bath in a closed flask connected with a hydrogen generator. The convicine dissolved. The mixture was allowed to stand under hydrogen for four days. On one day's standing, a few crystals could be seen around the edges of the liquid, and at the end of the fourth day a considerable quantity of quite large and well-formed alloxantin crystals had separated. The flask was cooled in ice water, opened and the contents filtered in a current of carbon dioxide through a filter paper into a 200-cc. volumetric flask. The residue on the paper was washed with ice water, the washings being collected in the 200-cc. flask. The crystals were then dried in a vacuum desiccator over sulfuric acid at room temperature. They weighed 0.4363 g., or 21.82% of the convicine taken.

Identification of Alloxantin.—The crystals turned violet-pink with ammonium hydroxide solution, and this solution turned deep blue on adding a little ferric chloride.

A crystallographic comparison with an authentic sample of alloxantin by Prof. W. E. Ford showed that the two were identical in crystal habit and refractive indices, and gave the same interference figure.

The crystals were recrystallized from boiling water in an atmosphere of carbon dioxide, dried and analyzed.

Anal. Calcd. for $C_8H_6N_4O_8 \cdot 2H_2O$: N, 17.40. Found: N, 17.62.

Determination of Ammonia Formed.—The contents of the 200-cc. volumetric flask were made to volume, and a 10-cc. aliquot was diluted, an excess of magnesium oxide and a small piece of paraffin added, and distilled into standard tenth-normal hydrochloric acid. The distillate was titrated with standard tenth-normal sodium hydroxide. Ammonia N found from 0.1000 g. of convicine, 0.00398 g., or 3.98%; per cent. total N in convicine, $C_{10}H_{15}N_3O_8 \cdot H_2O$, 13.00. The ammonia N is then 30.6% of the total N.

Identification of Dextrose.—The balance of the solution, not used for the ammonia determination, was treated with an excess of lead carbonate, filtered, and the residue washed with cold water. The filtrate and washings were saturated with hydrogen sulfide and the lead sulfide filtered and washed with water. The filtrate and washings from the lead sulfide were concentrated *in vacuo* on the water-bath to a small volume, filtered again and the concentration continued at room temperature in a vacuum desiccator. The solution, which was straw-colored until almost dry, turned to a deep red thick sirup.

This sirup was extracted ten times with boiling 95% alcohol, and the alcoholic extracts evaporated to dryness at room temperature in a vacuum desiccator. The residue was a clear scarlet sirup.

This sirup was dissolved in a little water, 1 cc. of 10% mercuric sulfate solution was added and the orange-pink precipitate was filtered and washed with water. The light yellow filtrate was made alkaline with barium hydroxide solution, saturated with carbon dioxide, filtered and the precipitate washed.

The clear pale straw-colored filtrate was evaporated in a vacuum desiccator over sulfuric acid at room temperature to constant weight; wt. of brownish-yellow sirup, 1.1035 g.

The sirup was dissolved in 10 cc. of water and a 2-cc. portion was heated with 0.2 g. of phenylhydrazine hydrochloride and 0.3 g. of sodium acetate in a boiling water-bath. In a few minutes the osazone began to crystallize out. After heating for an hour and a half, the reaction mixture was cooled and the osazone filtered and washed with water. Recrystallized once from 1:1 alcohol–acetone and once from 50% alcohol, it melted at 207–208°, and had the characteristic crystalline appearance of glucosazone. A mixed melting point with a known sample of glucosazone showed no depression. The weight of twice recrystallized material was 0.0506 g.

Portions of the sirup gave no color when heated with hydrochloric acid and resorcin and no violet-red color with hydrochloric acid and phloroglucinol.

The balance of the sirup was treated with nitric acid by the technique of van der Haar[16] for the isolation of potassium acid saccharate. A few crystals separated, but on recrystallizing till colorless their weight was only 2.8 mg.

Oxidation with Potassium Chlorate.—0.2000 g. of pure recrystallized convicine was mixed with 1.5 cc. of 1:1 hydrochloric acid, and 0.04 g. of potassium chlorate added in portions. The mixture was agitated from time to time. The convicine gradually dissolved. On standing overnight, the solution still smelled of chlorine. It was concentrated *in vacuo* at room temperature over stick potassium hydroxide to dryness. The residue was taken up in a little alcohol, filtered and the filtrate evaporated to dryness at room temperature *in vacuo*. The residue was taken up in a little water, made alkaline with sodium hydroxide and sodium picrate solution added. There was an odor of ammonia, but no trace of a precipitate.

The solution was diluted, acidified with hydrochloric acid and extracted with ether until there was no more color in the ether layer. The aqueous solution was then evaporated to dryness at room temperature over stick potassium hydroxide, taken up in 1 cc. of water, 3.5 cc. glacial acetic acid and 0.5 cc. of a 10% methyl alcoholic solution of xanthydrol added. A precipitate came down which under the microscope consisted of small needles clustered together at the ends. It was filtered, washed with alcohol and dried *in vacuo*.

Anal. Calcd. for dixanthylurea, $C_{27}H_{20}N_2O_3$: N, 6.67. Found: N, 6.88.

Reaction with Potassium Cyanate.[17]—0.526 g. of convicine was warmed to about 70° with a mixture of 15 cc. of glacial acetic acid and 5 cc. of absolute alcohol. It did not appear to dissolve. One gram of potassium cyanate was added in portions from time to time. There was no odor of hydrocyanic acid. The mixture was digested on the water-bath for two and one-half hours, the temperature rising to 79°. It was then allowed to stand overnight. The next day the insoluble matter was filtered off, washed with absolute alcohol and dried in a vacuum desiccator. It weighed 0.450 g., or 85.6% of the convicine taken. An analysis showed that it was unchanged convicine.

Anal. Calcd. for $C_{10}H_{15}N_3O_8 \cdot H_2O$: N, 13.00. N found in this sample of convicine, 12.31. N found in reaction product, 12.86.

Summary

1. The presence of convicine in broad beans (*vicia faba*), reported by Ritthausen, has been confirmed.

2. On acid hydrolysis convicine yields alloxantin, one molecule of ammonia and glucose which gives its corresponding glucosazone by interaction with phenylhydrazine.

3. Potassium chlorate oxidizes convicine with the formation of urea. No guanidine is formed.

4. Convicine did not react with potassium cyanate to form a urea derivative.

[16] A. W. van der Haar, "Anleitung zum Nachweis, etc., der Monosaccharide und Aldehydsäuren," Gebrüder Borntraeger, Berlin, 1920, p. 100.

[17] Bailey and Snyder, THIS JOURNAL, **37**, 935 (1915); Bailey and Read, *ibid.*, **37**, 1884 (1915); Bailey and Mikeska, *ibid.*, **38**, 1771 (1916); Bailey and Moore, *ibid.*, **39**, 279 (1917).

5. A structure for convicine is proposed. It is represented as a hexoside of 4-iminodialuric acid.

6. This research is being continued.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

TRIPHENYLVINYLMAGNESIUM BROMIDE

BY C. FREDERICK KOELSCH[1]

RECEIVED JANUARY 5, 1932 PUBLISHED MAY 7, 1932

During the course of an investigation on the unusual reactivity of the halogen in benzoyldiphenylmethyl bromide, a need was felt for a method by which substituted derivatives of the parent diphenylacetophenone could be prepared. It was thought that the enol forms of such ketones might be obtained by a reaction analogous to that sometimes used for the preparation of phenols, namely, by the oxidation of a properly chosen Grignard reagent. Such a Grignard reagent would have the —MgX group attached to an unsaturated carbon atom and would be of the type $RR'C{=}C(MgX)C_6H_5$, where R and R′ are aromatic radicals.

A compound of this type has not been prepared previously. The most closely related Grignard reagents are styrylmagnesium bromide[2] and β,β-diphenylvinylmagnesium bromide.[3] Whether or not the more highly substituted triphenylvinylmagnesium bromide could be obtained was a question which had to be settled by experiment. In the present paper it is shown that triphenylvinyl bromide forms a Grignard reagent, and some reactions of this compound are described.

A number of so-called negative results were obtained in the study of this Grignard reagent. With *dry air* or *oxygen*, a yellow ether-insoluble substance was formed, but decomposition of this with dilute acids gave a tarry oil from which no diphenylacetophenone could be obtained; on steam distillation of this tar no trace of benzophenone, which would be formed from a possible peroxide, $(C_6H_5)_2C(O_2)CC_6H_5(OMgBr)$, was obtained.

Thionyl chloride reacted vigorously to give an unworkable oil, while *benzyl chloride* was recovered nearly quantitatively after six hours' refluxing in ether; *triphenylchloromethane* was rapidly and completely converted into triphenylmethyl, isolated as the peroxide; the other product was a yellow ether-soluble glassy substance from which no crystalline material could be obtained. *Acetone* was apparently condensed by the reagent with the formation of mesityl oxide and triphenylethylene. *Benzophenone* gave a deep red solution, but carbonation followed by hydrolysis showed that the whole of the Grignard reagent was still present, and the ketone was recovered unchanged.

---

[1] National Research Fellow in Chemistry.

[2] Rupe and Proske, *Ber.*, **43**, 1231 (1910).

[3] Lipp, *ibid.*, **56**, 571 (1923); Ziegler, *ibid.*, **55**, 2257 (1922); Ziegler and co-workers, *Ann.*, **443**, 161 (1925); and previous papers.

More significant and interesting results were obtained when the Grignard reagent was treated with certain other substances.

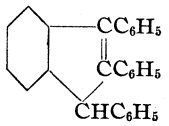
With *iodine*, triphenylvinyl iodide was obtained. Contrary to expectations, no iodide dichloride could be obtained from this compound. When a carbon tetrachloride solution of it was treated with chlorine, iodine was liberated immediately even at $-5°$.

Treatment of the Grignard reagent with *water* gave the hydrocarbon from which it is derived, triphenylethylene.

Formaldehyde gave β,γ,γ-triphenylallyl alcohol. This alcohol was etherified by allowing it to stand in methyl or ethyl alcoholic solution in the presence of sulfuric acid. The ethers obtained were also prepared from β,γ,γ-triphenylallyl bromide by boiling with the corresponding alcohol.[4]

Benzaldehyde gave $\alpha,\beta,\gamma,\gamma$-tetraphenylallyl alcohol, which, however, could not be obtained crystalline or pure enough for analysis. By treating this alcohol with sulfuric acid in acetic acid, the known 1,2,3-triphenylindene[5] was formed.

$$(C_6H_5)_2C{=}C(C_6H_5)CHOHC_6H_5 \xrightarrow{-H_2O}$$



Benzoyl chloride gave the long known triphenylacrylophenone $C_6H_5COC(C_6H_5){=}C(C_6H_5)_2$.

Benzoyl peroxide reacted vigorously to give the enol benzoate of diphenylacetophenone,[6] which was hydrolyzed to diphenylacetophenone by warming with alkali.

$$(C_6H_5)_2C{=}C(MgBr)C_6H_5 + (C_6H_5COO)_2 \longrightarrow (C_6H_5)_2C{=}C(OCOC_6H_5)C_6H_5 + C_6H_5COOMgBr;$$

$$(C_6H_5)_2C{=}C(OCOC_6H_5)C_6H_5 \xrightarrow{HOH} [(C_6H_5)_2C{=}C(OH)C_6H_5] \longrightarrow (C_6H_5)_2CHCOC_6H_5$$

In this indirect way the original object of this research was attained, but the reactions involved are impractical from a preparative standpoint.

Carbon dioxide gave triphenylacrylic acid, and *carbon disulfide* gave the sulfur analog, triphenylvinylcarbithionic acid, a beautifully crystalline red substance.

Experimental

Triphenylvinyl Bromide.—To a solution of 40 g. of triphenylethylene[7] in 250 ml. of glacial acetic acid was added with cooling 25 g. of bromine at such a rate that the temperature remained below 40°. The solution was distilled for a short time to drive off the hydrogen bromide, water was added almost to turbidity, and the solution was

[4] *Cf.* Meisenheimer, *Ann.*, **456**, 147 (1927).

[5] Kohler, *Am. Chem. J.*, **40**, 230 (1908).

[6] *Cf.* Gilman and Adams, THIS JOURNAL, **47**, 2816 (1925).

[7] Hell and Wiegandt, *Ber.*, **37**, 1431 (1904).

cooled. The product was pure after one washing with dilute acetic acid and melted at 114–115.5°; yield, 95–98%.

Triphenylvinylmagnesium Bromide.—Ten grams of triphenylvinyl bromide, 0.8 g. of magnesium, and a small crystal of iodine were covered with 200 ml. of dry ether, 0.05 ml. of ethyl bromide was added, and the mixture was refluxed. The reaction usually started within ten minutes; in even the most obstinate cases, reaction could be started by the addition of a small piece of magnesium separately etched with ethyl bromide. Nearly all of the magnesium was dissolved in less than two hours after the reaction had started. A U-shaped mercury seal closing the top of the condenser satisfactorily prevented the diffusion of air.

In most cases one-half the quantity of ether specified above was used. Then the reagent separated as a crystalline solid toward the end of the reaction, but its yield and its reactivity appeared to be unaffected.

Reaction with Iodine.—To the Grignard reagent from 10 g. of triphenylvinyl bromide was added solid iodine until the color was permanent. After hydrolysis with dilute sulfuric acid and removal of the ether, the product was crystallized from alcohol and finally from ligroin. There was obtained 6 g. of triphenylvinyl iodide which melted at 125–126°.

Anal. Calcd. for $C_{20}H_{15}I$: C, 62.8; H, 3.92. Found: C, 63.0; H, 3.94.

Reaction with Water.—Hydrolysis of the Grignard reagent from 10 g. of triphenylvinyl bromide gave 5 g. of triphenylethylene which boiled at 240–250° (33 mm.) and melted at 66–68°. This took up the calculated quantity of bromine to give triphenylvinyl bromide melting at 114–115°.

Reaction with Formaldehyde.—An excess of formaldehyde was led over the Grignard reagent from 5 g. of triphenylvinyl bromide. After the exothermic reaction was over, the product was decomposed with dilute ammonium chloride solution. Evaporation of the ether left a sirup which crystallized on rubbing with petroleum ether. Recrystallization from 50% ethanol gave 2.05 g. of β,γ,γ-triphenylallyl alcohol which melted at 126–128°, and was easily soluble in the common solvents. It gave a yellow solution in cold concd. sulfuric acid which became green on warming.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.29. Found: C, 88.0; H, 5.96.

α-Methoxy-β,γ,γ-triphenyl-β-propene.—A solution of 0.5 g. of β,γ,γ-triphenylallyl alcohol in 15 ml. of methanol containing 2 drops of concd. sulfuric acid was refluxed for fifteen minutes. The product crystallized out on cooling, and was recrystallized from methanol. It melted at 131–132.5°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.66. Found: C, 87.9; H, 6.35.

A mixed melting point showed the identity of the product with the one obtained when β,γ,γ-triphenylallyl bromide was boiled with methanol.

α-Ethoxy-β,γ,γ-triphenyl-β-propene.—The ethyl ether was prepared in the same way from β,γ,γ-triphenylallyl alcohol and ethanol. It melted at 125–128° alone or mixed with a sample of the same compound prepared according to the method of Meisenheimer.[4] Mixtures of the methyl and ethyl ethers or of either of these with the parent alcohol melted at 100–115°.

Reaction with Benzaldehyde.—To the Grignard reagent from 5 g. of triphenylvinyl bromide was added 1.6 g. of freshly distilled benzaldehyde. The crystalline magnesium compound which separated on standing was filtered off and decomposed with dilute sulfuric acid. An oil was obtained which could not be induced to crystallize. A portion (2.7 g.) was boiled for two minutes with 20 ml. of acetic acid containing 3 drops of concd. sulfuric acid. The 1,2,3-triphenylindene which crystallized out on cooling

weighed 2.3 g. and melted at 128–131°. Two recrystallizations from alcohol raised the melting point to 132–134°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.2; H, 5.82. Found: C, 94.1; H, 5.90.

A solution of 0.9 g. of the crude tetraphenylallyl alcohol in 15 ml. of methanol containing 2 drops of concd. sulfuric acid was allowed to stand at room temperature for six hours in an attempt to form a methyl ether, but again triphenylindene crystallized out.

Reaction with Benzoyl Chloride.—To the Grignard reagent from 10 g. of triphenylvinyl bromide was added 4 ml. of benzoyl chloride, and the mixture was refluxed for two hours. Hydrolysis with dilute sulfuric acid and removal of the ether left an oil which solidified on rubbing with alcohol. Recrystallization from ligroin gave 5 g. of triphenylbenzoylethylene which melted at 147–149° and whose melting point was not depressed by admixture with the same compound prepared by the method of Kohler.[8]

Reaction with Benzoyl Peroxide.—To the Grignard reagent from 5 g. of triphenylvinyl bromide was added slowly and with cooling 3.5 g. of finely powdered benzoyl peroxide. After forty-eight hours the mixture was decomposed with dilute sulfuric acid. Most of the triphenylvinyl benzoate crystallized from the ether layer. A total of 1.05 g. of the compound was obtained which after one recrystallization from alcohol melted at 151–153°. On boiling this for three minutes with a little 5% alcoholic potash there was obtained diphenylacetophenone which melted at 134–136° alone or mixed with an authentic sample.

Reaction with Carbon Dioxide.—Carbonation of the Grignard reagent from 10 g. of triphenylvinyl bromide was carried out in the usual way. After acid hydrolysis of the magnesium compound, the product was extracted from the ether layer with sodium carbonate solution, and was precipitated from this with hydrochloric acid. Crystallization from acetic acid gave 8.0 g. of triphenylacrylic acid which melted at 217–218° and gave the red diphenylindone melting at 151–152° on heating with zinc chloride.

Reaction with Carbon Disulfide.—To the Grignard reagent from 10 g. of triphenylvinyl bromide was added 2 ml. of carbon disulfide. The mixture slowly became orange in color and deposited a lemon-yellow crystalline substance. After forty-eight hours the ether was decanted, and the deposit was washed with a little dry ether. It was then dissolved in water. The addition of hydrochloric acid to the red solution obtained precipitated an oil which rapidly solidified. Crystallization from hot glacial acetic acid gave 4.7 g. of triphenylvinylcarbithionic acid which separated in the form of deep red plates that melted at 135°.

Anal. Calcd. for $C_{21}H_{16}S_2$: S, 19.3. Found: S, 19.4.

Summary

Triphenylvinyl bromide with magnesium forms a Grignard reagent. Although this compound does not react or reacts abnormally with some few substances, it gives normal products with iodine, water, formaldehyde, benzaldehyde, benzoyl chloride, benzoyl peroxide, carbon dioxide and carbon disulfide.

CAMBRIDGE, MASSACHUSETTS

[8] Kohler, *Am. Chem. J.*, **38**, 559 (1907).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

PHENYL-PARA-TOLYLACETOPHENONE

BY C. FREDERICK KOELSCH[1]

RECEIVED JANUARY 5, 1932 PUBLISHED MAY 7, 1932

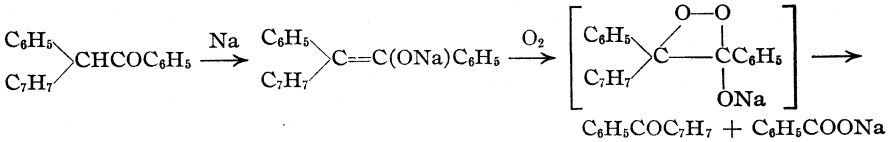
By the action of phenyl-*p*-tolylacetyl chloride on benzene in the presence of aluminum chloride, McKenzie and Widdows[2] obtained in poor yield a compound melting at 160° which they believed to be phenyl-*p*-tolylacetophenone. Recently McKenzie, Mills and Myles[3] by the dehydration of α,β-diphenyl-α-*p*-tolylethylene glycol obtained the isomeric *p*-diphenylacetotoluene which melted at 97–99.5°.

Needing some phenyl-*p*-tolylacetophenone, the writer essayed its preparation by the method of McKenzie and Widdows. All attempts, however, to duplicate the results of these authors were unsuccessful; the only product which could be isolated was diphenylmethane. This was quite surprising in view of the fact that diphenylacetyl chloride and toluene under the usual conditions of the Friedel–Crafts reaction were found to give an excellent yield of *p*-diphenylacetotoluene.

Phenyl-*p*-tolylacetophenone was finally obtained in nearly quantitative yield from toluene, desyl chloride, and aluminum chloride, but it melted at 98° and not at 160° as reported by McKenzie and Widdows. That the product actually had the structure assigned to it was shown by its reactions.

Cleavage by boiling with alcoholic potash gave benzoic acid and phenyl-*p*-tolylmethane.

Sodium in boiling toluene reacted slowly to give a sodium salt which was cleaved by oxygen, probably through an intermediate peroxide, into phenyl-*p*-tolyl ketone and sodium benzoate.[4]



$C_6H_5COC_7H_7 + C_6H_5COONa$

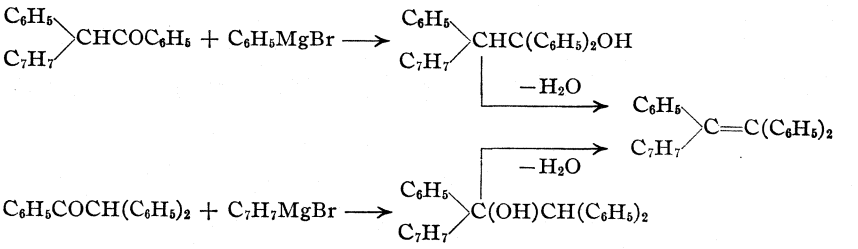
With phenylmagnesium bromide there was obtained a carbinol isomeric with the one obtained from *p*-tolylmagnesium bromide and diphenylacetophenone. Both of these carbinols gave triphenyl-*p*-tolylethylene on dehydration.

[1] National Research Fellow in Chemistry.

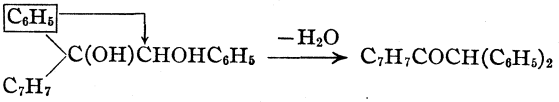
[2] McKenzie and Widdows, *J. Chem. Soc.*, **107**, 708 (1915).

[3] McKenzie, Mills and Myles, *Ber.*, **63**, 904 (1930).

[4] For analogous reactions see Kohler, *Am. Chem. J.*, **36**, 531 (1906); Staudinger, *Helv. Chim. Acta*, **5**, 663 (1922).



Since the melting point of phenyl-*p*-tolylacetophenone (98°) lies so close to that of the isomeric *p*-diphenylacetotoluene (101°), it seemed advisable to repeat the work of McKenzie, Mills and Myles on the dehydration of α,β-diphenyl-α-*p*-tolylethylene glycol, especially since the radical wandering necessary for the formation of *p*-diphenylacetotoluene is so unexpected.[5]



The reaction was found to take this course. The product melted at 101° alone or mixed with *p*-diphenylacetotoluene, while a mixture with phenyl-*p*-tolylacetophenone had a much lower and an unsharp melting point.

In agreement with the observation of Anschütz and Förster,[6] desyl chloride and benzene in the presence of aluminum chloride gave diphenylacetophenone. The yield was good, and this is probably the best of the many methods which have been used for the preparation of this compound.

Experimental

***p*-Diphenylacetotoluene.**—Ten grams of diphenylacetic acid was warmed with 8 ml. of thionyl chloride, and when the reaction was finished the excess of thionyl chloride was distilled under reduced pressure from a bath at 85°. The diphenylacetyl chloride remaining was dissolved in 20 ml. of pure toluene and added slowly with shaking and ice cooling to 10 g. of anhydrous aluminum chloride in 70 ml. of toluene. The solution was boiled as long as hydrogen chloride, which was not evolved in the cold, was given off (thirty minutes), and then to the cooled solution was added iced dilute hydrochloric acid. The pale yellow toluene layer was steam distilled, leaving a solid residue. This was crystallized twice from alcohol, giving 9.1 g. of pure diphenylacetotoluene melting at 100–101° (McKenzie, Mills and Myles give 97–99.5°).

The same compound was prepared in about 20% yield from diphenylacetyl chloride and *p*-tolylmagnesium bromide according to the procedure used by Orékhoff[7] for carrying out the reaction between diphenylacetyl chloride and phenylmagnesium bromide.

[5] Lagrave [*Ann. Chim.*, [10] **8**, 363 (1927)] in studying the rearrangement of ethylene oxides of the type $R\overline{CH—O—C}(C_6H_5)_2$ has reached the conclusion (p. 383, line 10) that the migratory tendency of hydrogen is greater than that of R, except (p. 366) when R is *p*-anisyl.

[6] Anschütz and Förster, *Ann.*, **368**, 93 (1909); *cf.* McKenzie and Lesslie, *Ber.*, **61**, 158 (1928).

[7] Orékhoff, *Bull. soc. chim.*, [4] **25**, 189 (1919).

Phenyl-*p*-tolylacetophenone.—To a solution of 25 g. of desyl chloride[8] in 150 ml. of toluene was added with cooling 16 g. of anhydrous aluminum chloride in small portions. The mixture, which evolved hydrogen chloride slowly in the cold, was refluxed for thirty minutes, cooled and decomposed with iced hydrochloric acid. Steam distillation of the toluene layer left a yellow residue which became solid on cooling. Crystallization from alcohol gave 24 g. melting at 94–95° which was still slightly colored. Recrystallization from benzene–ligroin gave a pure white product melting at 97–98°. The substance distilled undecomposed at 270–275° (29 mm.).

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.0; H, 6.30. Found: C, 87.8; H, 6.33.

Diphenylacetophenone.—Twenty-five grams of desyl chloride, 125 ml. of benzene, and 16 g. of aluminum chloride refluxed for fifteen minutes gave diphenylacetophenone, which after one crystallization from acetic acid melted at 135–136° and weighed 23 g.

Cleavage of Phenyl-*p*-tolylacetophenone with Alkali.—Ten grams of phenyl-*p*-tolylacetophenone was refluxed for five hours with a solution of 5 g. of potassium hydroxide in 60 ml. of alcohol. Most of the alcohol was then distilled, and the residue was steam distilled. From the distillate was obtained 3.8 g. of phenyl-*p*-tolylmethane boiling at 275–280°; from the non-volatile part there was obtained 2.5 g. of benzoic acid, identified by melting point and neutral equivalent. There was recovered 3.8 g. of unchanged ketone.

Cleavage of the Sodium Salt with Oxygen.—A solution of 10 g. of phenyl-*p*-tolylacetophenone in 75 ml. of dry toluene was refluxed with 0.8 g. of sodium. A pale yellow flocculent substance appeared as the metal reacted, and after six hours no more sodium was present. Dry air was then aspirated through the cooled suspension for two hours. Washing with water removed sodium benzoate, from which there was obtained 2.75 g. (65%) of benzoic acid. The non-aqueous layer, after the toluene was steam distilled, gave 3.5 g. of phenyl *p*-tolyl ketone boiling at 190–210° (35 mm.) and melting at 52° (mixed melting point). This cleavage product was further identified by the formation of diphenyl-*p*-tolylcarbinol melting at 69–70° from it and phenylmagnesium bromide.

α,α,β-Triphenyl-β-*p*-tolylethanol.—Six grams of phenyl-*p*-tolylacetophenone was added to the Grignard reagent from 7.9 g. of phenyl bromide. After refluxing for thirty minutes, the solution was decomposed with iced ammonium chloride. The residue after removal of the ether was boiled out with alcohol, and the undissolved part was crystallized from ligroin (80–110°) and then from methanol, giving 1.2 g. which melted at 169–170°.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.9; H, 6.58. Found: C, 88.7; H, 6.27.

α,β,β-Triphenyl-α-*p*-tolylethanol.—The reaction product from 5.5 g. of diphenyl acetophenone and the Grignard reagent from 9 g. of *p*-tolyl bromide was worked up in the usual way, giving 1.2 g. which melted at 185–187°. (McKenzie, Mills and Myles[3] give 180–181° for the compound prepared from *p*-diphenylacetotoluene and phenylmagnesium bromide.)

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.9; H, 6.58. Found: C, 88.8; H, 6.40.

α,α,β-Triphenyl-β-*p*-tolylethylene.—Eight-tenths of a gram of α,α,β-triphenyl-β-*p*-tolylethanol was refluxed for one hour with 10 ml. of acetyl chloride. The product was crystallized from acetic acid, giving 0.55 g. of the hydrocarbon, which melted at 150–151°.

Anal. Calcd. for $C_{27}H_{22}$: C, 93.6; H, 6.35. Found: C, 93.4; H, 5.90.

The dehydration of α,β,β-triphenyl-α-*p*-tolylethanol was carried out in the same way. A mixed melting point showed the identity of the products.

[8] Prepared according to Schroeter and Caspar, *Ber.*, **42**, 2348 (1909).

Summary

Phenyl-*p*-tolylacetophenone could not be prepared from phenyl-*p*-tolylacetyl chloride and benzene, but it was obtained from desyl chloride and toluene. It reacted normally with phenylmagnesium bromide, and it gave a sodium salt which oxygen cleaved into phenyl *p*-tolyl ketone and sodium benzoate.

The work of McKenzie, Mills and Myles on the dehydration of α,β-diphenyl-α-*p*-tolylethylene glycol has been repeated and confirmed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

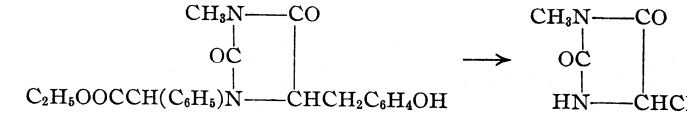
THE HYDROGEN CHLORIDE ADDITION PRODUCTS OF TYROSINE N-PHENYLACETIC ACID AND OF THE CORRESPONDING METHYL AND ETHYL ESTERS

BY DOROTHY A. HAHN AND ANNE L. WHITE[1]

RECEIVED JANUARY 6, 1932 PUBLISHED MAY 7, 1932

The following account of certain transformations of the N-phenylacetic acid derivative of tyrosine, $NH(CHC_6H_5COOH)CH(CH_2C_6H_4OH)COOH$, represents a continuation of work previously reported.[2] The imino dibasic acid was prepared by the same general method that has already been described,[3] but due to the fact that larger quantities of material were used in the reactions, a few additional facts in regard to this preparation need to be noted.

It was found, for example, during the process of digesting 50 g. of ethyl N-3-methyl-5-anisalhydantoin-N-1-phenylacetate[4] with hydrogen iodide and then hydrolyzing the product with barium hydroxide, that a slight amount of decomposition had taken place in the sense



The decomposition product, N-3-methyl-5-*p*-hydroxybenzylhydantoin, was found mixed with the imino dibasic acid in the filtrate from the barium sulfate. Both substances separated in crystalline condition on concentrating the solution and were readily separated due to the fact that the hydantoin is very soluble in hot water while the imino acid is relatively insoluble. After several recrystallizations from water the hydantoin was

[1] This work was offered in partial fulfilment of the requirements for the degree of Master of Arts at Mount Holyoke College.

[2] Hahn and Dyer, THIS JOURNAL, **52**, 2494 (1930).

[3] Hahn and Dyer, *ibid.*, p. 2503.

[4] Hahn and Dyer, *ibid.*, p. 2497.

analyzed and finally identified by comparison with a specimen of N-3-methyl-5-*p*-hydroxybenzylhydantoin which had been synthesized according to the method described by Johnson and Nicolet.[5]

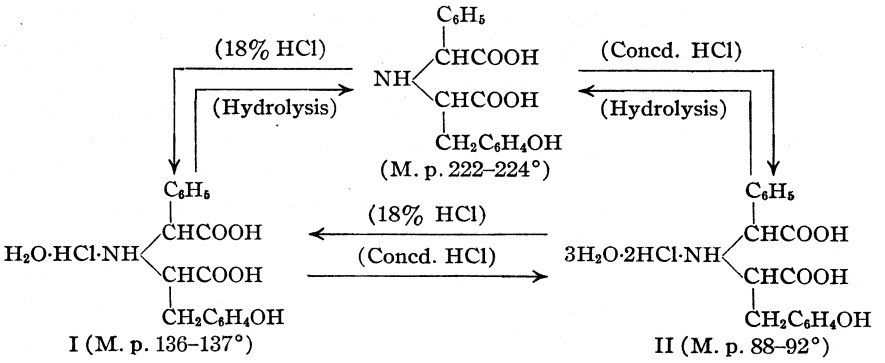
Due to the relatively great insolubility of the imino dibasic acid in boiling water, considerable difficulty was experienced at first in attempting to prepare it in quantity. For example, when starting with 50 g. of ethyl N-3-methyl-5-anisalhydantoin-N-1-phenylacetate and proceeding in the usual way,[6] it was found convenient to precipitate the barium sulfate in approximately one liter of boiling solution. The filtrate under these conditions when concentrated was found to yield only about 2–3 g. of the imino acid, the bulk of the product being retained along with barium sulfate as an insoluble white precipitate. The fact that one gram of imino acid requires about 500 cc. of boiling water for solution made the matter of separating it from the barium sulfate extremely difficult. The problem was finally solved by extracting the barium sulfate with small quantities of boiling aqueous hydrochloric acid (18%). Under these conditions the imino acid reacted to form the corresponding hydrochloride, which is very soluble in boiling acid of this concentration and only slightly soluble in the cold solution. The hydrochloride, which separates in well-defined crystals and is readily purified by recrystallization from aqueous hydrochloric acid, is further characterized by the fact that it dissociates hydrogen chloride when boiled with water, passing quantitatively into the free imino dibasic acid. If the precaution is taken of first extracting the barium sulfate precipitate with boiling alcohol to remove all traces of organic coloring matter, approximately 65% of the amount of imino acid required by theory may be obtained in exceptionally pure condition by then extracting the barium sulfate precipitate with aqueous hydrochloric acid in the manner just described.

The N-phenylacetic acid derivative of tyrosine reacts with aqueous hydrochloric acid to form two different addition products melting at 136–137° and 88–92°, respectively, with the evolution of a gas. They represent the addition of one and two molecules of hydrochloric acid to one molecule of imino acid, and separate, respectively, from dilute and concentrated solutions of hydrochloric acid. Of the two the first represents the more stable form but each may be readily transformed into the other and also be hydrolyzed to the free imino acid. These relationships are shown by means of the chart.

The hydrochloride, I, $C_{17}H_{17}O_5N \cdot HCl \cdot H_2O$, **m. p. 136–137°, was prepared by dissolving 7.0 g. of imino acid, m. p. 222–224°, in 15 cc. of boiling 18% aqueous hydrochloric acid. The clear solution on cooling deposited 6.9 g. of fine white crystals which melted at 136–137°. An additional 0.8 g. was obtained by concentrating the mother liquor, thus bringing the yield up to approximately the amount required by theory.**

[5] Johnson and Nicolet, *Am. Chem. J.*, **47**, 470 (1912).

[6] Hahn and Dyer, *ibid.*, **52**, 2503 (1930).



The substance was purified by recrystallization from hot 18% aqueous hydrochloric acid in which it is extremely soluble (1 g. in 1.5 cc.) and from which it separates on cooling in clusters of small hard white crystals which form on the bottom of the beaker.

Anal. Calcd. for $C_{17}H_{17}O_5N \cdot HCl \cdot H_2O$: N, 3.79; Cl, 9.61. Found: N, 3.79, 3.85; Cl, 9.53, 9.57.

Although the analyses indicate the presence of water of crystallization, it was impossible to determine this separately because of the fact that the substance dissociates hydrochloric acid on heating. Solution in alcohol or water produces the same effect but under these conditions quantitative yields of the free imino dibasic acid are obtained as a result of the hydrolysis. When concentrated hydrochloric acid, sp. gr. 1.18, is added to solutions of this hydrochloride in hot aqueous 18% hydrochloric acid, the mixture on cooling deposits a white crystalline precipitate which melts at 88–92° and which represents the second modification referred to above.

The hydrochloride, II, $C_{17}H_{17}O_5N \cdot 2HCl \cdot 3H_2O$, m. p. 88–92°, was prepared by adding 4.5 cc. of concentrated hydrochloric acid, sp. gr. 1.18, to a solution of 2.0 g. of imino acid, m. p. 222–224°, in 9 cc. of hot 18% aqueous hydrochloric acid. Under these conditions a substance crystallizing in long soft white needles and filling the entire space occupied by the solution separated on cooling. The product consisted of 1.8 g., m. p. 88–92°, and corresponded to a yield of 64% of the theoretical. On concentrating the mother liquor, 0.25 g. of the hydrochloride, I, m. p. 136–137°, was deposited.

In order to recrystallize the hydrochloride, II, m. p. 88–92°, it was always necessary to dissolve it in hot 18% aqueous hydrochloric acid and treat the solution with twice its volume of concentrated hydrochloric acid, sp. gr. 1.18. After purification by several recrystallizations, the melting point was found to remain constant, 88–92°, with the evolution of a gas.

Here again it was found to be impossible to dehydrate the substance before making the analyses since decomposition begins at about 90°. The results of analysis would seem to indicate, however, that three molecules of water are held in the form of water of crystallization.

Anal. Calcd. for $C_{17}H_{17}O_5N \cdot 2HCl \cdot 3H_2O$: N, 3.17; Cl, 16.07. Found: N, 3.18, 3.20; Cl, 16.05, 15.93.

The hydrochloride, m. p. 88–92°, is extremely soluble in alcohol but cannot be obtained from this solvent in crystalline form since it separates as a gummy mass on concentrating the solution. The substance is also very soluble in water but hydrolyzes immediately to give the free imino acid, which separates as a flocculent precipitate. The transformation to the free acid may be carried out almost quantitatively by boiling 4.0 g. of the hydrochloride with 50 cc. of water for an hour. The substance is very

soluble in hot 18% aqueous hydrochloric acid (1 g. in 1.8 cc.) and less soluble in hot concentrated hydrochloric acid, sp. gr. 1.18 (1 g. in 10 cc.).

This hydrochloride is of interest because of the fact that it is extremely unstable, tending to dissociate hydrochloric acid under a variety of different conditions. For example, when a sample of the substance was dissolved in 18% aqueous hydrochloric acid and the solution allowed to cool, the product was found to lose one molecule of hydrochloric acid, passing quantitatively into the hydrochloride, I, m. p. 136–137°. The same general effect was produced by heating the dry crystals, m. p. 88–92°, in a test-tube at a temperature of 80°. In this case the evolution of hydrogen chloride gas was demonstrated by collecting the gas in water and testing the solution with silver nitrate. That the substance dissociates hydrochloric acid even on standing in the air at ordinary temperatures has also been demonstrated, the change having been followed by means of melting point determinations and analyses for chlorine. For example, a sample, m. p. 88–92°, was allowed to stand in a stoppered bottle for five months. At the end of this time the melting point had changed from 88–92° to 93–138°, approaching the melting point of the hydrochloride I. In analyzing for halogen it was found that a freshly prepared sample showed 15.93 and 16.05% of chlorine while a specimen that had stood in a stoppered bottle for two months gave 15.88% and 15.82%. The same specimen was then allowed to stand in an open bottle in a desiccator and was analyzed three days later, when the percentage of chlorine was found to have dropped to 15.74 and 15.70%.

The diethyl ester hydrochloride of the imino acid[7] was readily prepared by dissolving 7.7 g. of imino acid, m. p. 222–224°, in 100 cc. of absolute alcohol which had been saturated with dry hydrogen chloride gas. The mixture, after heating on a steam-bath for five hours, with a reflux condenser, was concentrated to one-third its original volume and allowed to cool. Since no precipitate formed under these conditions, 60 cc. of dry ether was added, when a gum separated out which gradually became crystalline on standing. The product, which was filtered and washed with a little alcohol–ether mixture, weighed 2.2 g. and melted at 160–162° with the evolution of a gas. Purified by recrystallization from absolute alcohol–ether mixtures (1:3), the melting point changed to 161–162° with the evolution of a gas.

Anal. Calcd. for $C_{21}H_{25}O_5N \cdot HCl$: N, 3.44. Found: N, 3.44, 3.43.

This substance is extremely soluble in alcohol, dissolving in less than its own volume of the solvent. It is insoluble in ether and may be precipitated from alcohol solution by the addition of about three volumes of ether.

When treated with water it undergoes hydrolysis and an oil separates at once. The aqueous solution, when decanted, was found to contain hydrochloric acid.

The corresponding dimethyl ester hydrochloride, m. p. 180–180.5°, was prepared according to Fischer's esterification method.

For example, 10 g. of imino acid, m. p. 222–224°, was dissolved by warming with 50 cc. of a saturated absolute methyl alcohol solution of hydrogen chloride. After heating the mixture with a reflux condenser, the alcohol was distilled off under reduced pressure and the process repeated until the gummy residue remaining in the flask after the distillation of alcohol finally changed into a hard brittle mass. This was then dissolved in 30 cc. of a saturated absolute methyl alcohol solution of hydrogen chloride and 30 cc. of ether added. Under these conditions the solution became cloudy and on standing a crystalline precipitate was formed. The product obtained in this way when filtered and washed with a small quantity of an absolute methyl alcohol–ether mixture (1:1) weighed 6.0 g. and melted at 177–180°. Additional quantities of this substance were obtained on concentrating the mother liquor and then adding ether. When purified by recrys-

[7] Acknowledgment is made to Elizabeth Dyer for preparation of this substance.

tallization from absolute methyl alcohol–ether mixtures, it separates in the form of very fine white needles which melt at 180–180.5° with the evolution of a gas.

Anal. Calcd. for $C_{19}H_{21}O_5N \cdot HCl$: N, 3.69; Cl, 9.37. Found: N, 3.67, 3.68; Cl, 9.32, 9.29.

The dimethyl ester hydrochloride is extremely soluble in absolute methyl alcohol, dissolving in less than its own volume, and is insoluble in ether. While stable in alcohol–ether mixtures, it readily dissociates hydrochloric acid when dissolved in water. Solution in this solvent is accompanied by the immediate separation of an oil and the water layer when decanted gives a precipitate of silver chloride when tested in the usual way.

Summary

An improved method for separating and purifying tyrosine-N-phenylacetic acid is described. Two distinct hydrogen chloride addition products of this acid have been prepared, together with the hydrochlorides of the corresponding methyl and ethyl esters.

SOUTH HADLEY, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHEKIANG, CHINA]

RESEARCHES ON PYRIMIDINES. CXXVIII. THE REARRANGEMENT OF 2-ETHYLMERCAPTO-4-METHYL-6-THIOCYANOPYRIMIDINE INTO ITS ISOTHIOCYANATE MODIFICATION[1,2]

BY YUOH FONG CHI AND YUN HWANG CHEN

RECEIVED JANUARY 6, 1932 PUBLISHED MAY 7, 1932

Since Wheeler, Johnson and their co-workers began the study of the chemistry of thiocyanopyrimidine compounds,[3] no specific change has proved to be more interesting to the writers than the rearrangement of 2-ethylmercapto-5-carbethoxy-6-thiocyanopyrimidine into its isomeric isothiocyanate modification, a transformation which was described recently in a paper by Johnson and Chi.[4] They found that this thiocyanate could be distilled without decomposition and without molecular conversion to the isothiocyanate form, while its molecular rearrangement into the isothiocyanate form could be accomplished easily, under specific experimental conditions, at a temperature much below that of its boiling point.

[1] This publication is a report of one phase of a research program dealing with the chemistry of certain pyrimidine thiocyanates, which was started originally in the Sterling Chemistry Laboratory of Yale University under the direction of Professor Treat B. Johnson.

[2] This research has been accomplished and arranged for publication through the support of a grant of $750 from the Rockefeller Foundation. The authors desire to express here their appreciation and heartiest thanks for this liberal assistance.

[3] Wheeler and Bristol, *Am. Chem. J.*, **33**, 450 (1905); Johnson and McCollum, *ibid.*, **36**, 143 (1906); Johnson and Storey, *ibid.*, **40**, 131 (1908).

[4] Johnson and Chi, THIS JOURNAL, **52**, 1580 (1930).

This behavior was so interesting that the writers decided to examine the stability of another pyrimidine representative which has not been investigated. We now find that a similar behavior is observed in the case of the molecular rearrangement of 2-ethylmercapto-4-methyl-6-thiocyanopyrimidine (I) into its isomeric form represented by formula II.

$$\overline{\overline{NC(SC_2H_5)=NC(CH_3)=CHC}}SCN \qquad \overline{\overline{NC(SC_2H_5)=NC(CH_3)=CHC}}NCS$$

I II

This thiocyanopyrimidine I exhibits a chemical behavior similar to Johnson and Chi's 2-ethylmercapto-5-carbethoxy-6-thiocyanopyrimidine. It can be distilled under diminished pressure (b. p. 155–158° at 5 mm.) without decomposition and without conversion into its isothiocyanate form II. The stability of the pyrimidine I, however, is greatly influenced by the presence of other reagents, and a molecular rearrangement to the isothiocyanate II can be accomplished easily at a temperature very much below that of the boiling point of the thiocyanate. This instability of molecular structure is quite remarkable. The conditions under which the transformation is brought about are described in the experimental part of this paper.

It has been the previous experience in the pyrimidine thiocyanate researches that thiocyanates corresponding to I may lead to the formation of polymeric forms of the thiocyanate after continued distillation.[5] These new constructions result from the polymerization of the isothiocyanate modification resulting by molecular rearrangement. In the case of the thiocyanate I, this polymerized form is not produced directly by distillation, but it is formed by prolonged heating of the rearranged form II. The polymer is distinguished from the isothiocyanate form by its nonreactivity toward ammonia, aniline and ethyl alcohol.

Experimental Part

2-Ethylmercapto-4-methyl-6-thiocyanopyrimidine. I.—This pyrimidine is easily prepared as follows: 20 g. of the corresponding chloropyrimidine[6] and 11 g. of potassium thiocyanate are dissolved in 120 cc. of 95% alcohol and the solution heated to boiling for one hour. The solution is then filtered hot to separate potassium chloride and then cooled, when the thiocyanate separates immediately in the form of colorless crystals. The yield was 19 g. or 81%. It was purified by crystallization from alcohol, melts at 69–70° to a clear liquid, and boils at 155–158° under 5 mm. pressure. The thiocyanate is insoluble in alkali, soluble in benzene, toluene and xylene. It is very soluble in hot alcohol, and insoluble in ether.

Anal. Calcd. for $C_8H_9N_3S_2$: N, 19.90. Found: N, 20.01, 19.62, 19.63.

This same thiocyanate compound I is likewise formed by refluxing 2-ethylmercapto-4-methyl-6-chloropyrimidine with potassium thiocyanate in both toluene and xylene solutions for one hour. The thiocyanate can be crystallized repeatedly from alcohol

[5] Johnson and Storey, *Am. Chem. J.*, **40**, 131 (1908).

[6] Johns, *ibid.*, **40**, 350 (1908).

without conversion to a thionurethan; it does not undergo any change leading to the formation of thioureas when exposed to the action of ammonia and aniline.

Molecular Rearrangement of the Thiocyanate I

2-Ethylmercapto-4-methyl-6-isothiocyanopyrimidine. II.—Four grams of the thiocyanate I was refluxed in 10 cc. of xylene for eight hours, giving a red colored solution. After distilling off the xylene, the isothiocyanate residue was triturated with cold ether and the ether finally evaporated, leaving behind the crude isothiocyanate as a red oil. This showed no signs of solidifying, and the yield corresponded to 67% of the theoretical. When this oil was subjected to distillation under diminished pressure, it slowly underwent a profound decomposition. A fraction distilling at 146–158° at 1 to 3 mm. exhibited all the properties of a true isothiocyanate. This reacted immediately with aniline, ammonia and alcohol in accordance with its isothiocyanate structure. Notwithstanding this characteristic behavior the oil did not respond to a good analysis for nitrogen and it could not be purified by further distillation.

Anal. Calcd. for $C_8H_9N_3S_2$; N, 19.90. Found: N, 21.00, 21.05.

Formation of the Polymerized Form of the Isothiocyanate.—Twenty grams of the thiocyanate I was treated as in the previous experiment to accomplish rearrangement to the isothiocyanate form. Attempts to purify the rearrangement product by distillation under diminished pressure led to the formation of a mixture of compounds. At 150–180° under a pressure of 4 to 10 mm., the impure isothiocyanate was collected. The distillation was then continued until the temperature rose to 220°, when a viscous oil was obtained which solidified almost immediately in the receiver. This dissolved in boiling benzene and separated on cooling in colorless crystals melting at 108–109°. The same crystalline compound was also obtained by redistillation of the crude isothiocyanate fraction boiling at 150–180° (see above). This substance is apparently a polymerized form of the isothiocyanate II. It can be recrystallized from alcohol without change, and does not combine with aniline and ammonia to form the corresponding thiourea derivatives.

Anal. Calcd. for $(C_8H_9N_3S_2)_x$: N, 19.90; S, 30.3. Found: N, 20.2, 20.00; S, 30.4.

Proof of Structure of the Isothiocyanate II

2-Ethylmercapto-4-methyl-6-thioureapyrimidine, $C_8H_{12}N_4S_2$.—The thiocyanate I was rearranged into the isothiocyanate form II, and an ether solution of the latter combined with an excess of concentrated aqueous ammonia. The corresponding thiourea was formed immediately and 1.8 g. of this was obtained from 2 g. of the thiocyanate. It was purified by crystallization from alcohol and melted at 229–231°.

Anal. Calcd. for $C_8H_{12}N_4S_2$: N, 24.55. Found: N, 24.35, 24.42.

2-Ethylmercapto-4-methyl-6-phenylthioureapyrimidine, $C_{14}H_{16}N_4S_2$.—Two grams of the rearranged thiocyanate gave 2.8 g. of this compound by treatment with aniline at ordinary temperature. This was purified by crystallization from 95% alcohol and separated in prisms melting at 209–210°.

Anal. Calcd. for $C_{14}H_{16}N_4S_2$: N, 18.41. Found: N, 18.28, 18.32.

2-Ethylmercapto-4-methyl-6-thionethylurethan Pyrimidine, $C_{10}H_{15}ON_3S_2$.—This is formed by warming the crude isothiocyanate II with absolute alcohol. The urethan separates from alcohol in the form of flat prisms melting at 97–98°.

Anal. Calcd. for $C_{10}H_{15}ON_3S_2$: N, 16.33. Found: N, 16.27, 16.31.

2-Ethylmercapto-4-methyl-6-thionmethylurethan Pyrimidine, $C_9H_{13}ON_3S_2$.—Prepared by the action of methyl alcohol on the crude isothiocyanate II. It crystallizes from ethyl alcohol in the form of needles melting at 84–86°.

Anal. Calcd. for $C_9H_{13}ON_3S_2$: N, 17.28. Found: N, 17.30.

Experimental Conditions Influencing the Rearrangement of the Pyrimidine Thiocyanate I

A.—Heating of the thiocyanate I at 115–120° for four hours and at 100° for eight hours did not give any detectable amount of the isothiocyanate modification.

Digestion of the pyrimidine thiocyanate I in toluene did not produce a rearrangement but the change was brought about by refluxing in xylene solution.

B. **Rearrangement of the Thiocyanate I by Heating with Alcohol.**—At the boiling point of ethyl alcohol the pyrimidine thiocyanate I undergoes no change and can be recrystallized repeatedly from this solvent without structural alteration. On the other hand, when heated in alcohol solution at 100° for six hours (55° below its boiling point), the thiocyanate is transformed completely into the isothiocyanate II, and the latter combines with the alcohol, giving the corresponding thionurethan. The yield is excellent, and the thionurethan melts sharply after one crystallization at 97–98°.

Summary

1. 2-Ethylmercapto-4-methyl-6-thiocyanopyrimidine is formed by interaction of potassium thiocyanate with 2-ethylmercapto-4-methyl-6-chloropyrimidine in boiling ethyl alcohol solution.

2. This thiocyanate distils at 155–158° at 5 mm. and is rearranged to its isomeric form, the isothiocyanate, (1) by heating with alcohol at 100° and (2) by digestion in boiling xylene.

3. 2-Ethylmercapto-4-methyl-6-isothiocyanopyrimidine cannot be distilled without decomposition. It is slowly transformed into a polymeric modification.

4. The thiocyanate does not react with alcohols, ammonia or aniline. The isothiocyanate interacts with these same reagents to form the corresponding thionurethans and thioureas, respectively.

HANGCHOW, CHEKIANG, CHINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MARYLAND]

THE PARA-PHENYLPHENACYL ESTERS OF CERTAIN ORGANIC ACIDS[1]

BY NATHAN L. DRAKE AND JAMES P. SWEENEY

RECEIVED JANUARY 6, 1932 PUBLISHED MAY 7, 1932

The advantages of *p*-phenylphenacyl bromide as a reagent for identifying organic acids have been previously described by Bronitsky and one of us.[2] We have made frequent use of the reagent in this Laboratory in research and in a course in organic qualitative analysis, and because of the success we have experienced in its use, we have deemed it desirable to report the melting points and solubility behavior of certain *p*-phenylphenacyl esters not prepared in the earlier work.

[1] From a thesis submitted to the Graduate School of the University of Maryland by J. P. Sweeney in partial fulfilment of the requirements for the degree of Master of Science.

[2] Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

Judefind and Reid[3] found that *p*-bromophenacyl bromide did not yield esters smoothly with dibasic acids; however, from phenacyl bromide, Rather and Reid[4] were able to prepare satisfactorily the esters of succinic and glutaric acids. They did not attempt to prepare esters of any of the other dibasic acids.

p-Phenylphenacyl bromide, was found to yield esters smoothly with all the members of the α,ω-dibasic acid series from malonic acid to sebacic acid.

Experimental

Preparation of the Reagent.—The reagent was prepared as previously described.[2] In order to obtain a colorless *p*-phenylacetophenone with a minimum of effort, it has been found essential to wash the crude ketone obtained from the decomposition of the Friedel–Crafts addition product very carefully until entirely free from acid. If this precaution is taken, one or two crystallizations from alcohol are sufficient to give a colorless product with the correct melting point. Similarly in the preparation of the bromide, it is essential that *all* the acid be washed out of the crude material before recrystallization. One recrystallization from hot 95% alcohol is then sufficient to yield a pure colorless product. If these simple precautions are not observed, much difficulty will be encountered in obtaining a satisfactory reagent.

TABLE I

RESULTS OBTAINED

Acid	Melting or decomposition point of *p*-phenylphenacyl ester	Solvent for recrystallization
Malonic	175 (dried at 100 °C.)	Alcohol
Glutaric	152	Acetone
Adipic	148	Acetone
Pimelic	145–148 dec.	Alcohol
Suberic	151	Acetone
Azelaic	141	Acetone
Sebacic	140	Acetone
Phenylacetic	63 dec.	Alcohol
Hydrocinnamic	95	Alcohol
Isocaproic	70	Alcohol
Tartaric	203–204 dec.	Alcohol
p-Nitrobenzoic	182	Benzene
3,5-Dinitrobenzoic	154	Benzene
o-Bromobenzoic	98	Alcohol
Salicylic	148 (dried at 100 °C.)	Alcohol
p-Hydroxybenzoic	240	Acetone
o-Methoxybenzoic	131	Alcohol
Anisic	160	Alcohol
Gallic	195–198 dec.	Aq. alcohol
o-Phthalic	167.5	Alcohol
4-Nitrophthalic	120	Benzene
Tetrachlorophthalic	193	Acetone
Benzilic	122	Alcohol

[3] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

[4] Rather and Reid, *ibid.*, **41**, 75 (1919).

Preparation of the Esters.—The method used was similar to that employed in the former work, but it was found more convenient to use a solution of 1 *N* sodium hydroxide for neutralization of the acid, taking care to have the final salt solution slightly acid to prevent formation of colored by-products. The neutral equivalent of an unknown acid may thus be obtained with no additional effort.

The sodium salts of some of the dibasic acids were found to be insoluble in aqueous alcohol, and caused trouble. Mere substitution of the ethyl ammonium salt for the sodium salt did not obviate the difficulty. If, however, the acid was dissolved in a little water and neutralized with ethylamine, alcohol could be added until the salt started to come out of solution. By use of salts prepared in this way it was possible to obtain the di-esters satisfactorily; 0.0025 mole of acid and 0.005 mole of reagent were used in the experiments with dibasic acids.

Many of the esters listed below were found to be sparingly soluble in 95% alcohol, and accordingly their solubility was tested in acetone, ether and benzene.

Melting points were taken in a small beaker containing concd. sulfuric acid which was well stirred during the determination. No corrections were applied to the melting points, but the thermometer used was calibrated, and registered correctly at 0, 100 and 121.25°, the melting point of pure benzoic acid.

With but two acids were we unable to obtain satisfactory results. The ester of methylanthranilic acid was a gum which could not be induced to crystallize, and the ester of trinitrobenzoic acid was a red colloid which could not be filtered. It was also found that under the conditions used in this work, no esters were obtainable from sulfonic acids.

Summary

A number of common acids have been characterized by the preparation of their *p*-phenylphenacyl esters.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

PENTHIAZOLINES. I. THE ACTION OF HALOGENS ON THE DIMETHYL MALONATE ADDITION PRODUCT OF ALLYL MUSTARD OIL[1]

BY DAVID E. WORRALL

RECEIVED JANUARY 7, 1932 PUBLISHED MAY 7, 1932

It has been shown previously that the aromatic isothiocyanates react smoothly with certain esters[2] containing an active methylene group, forming substituted thioamides that have been found useful for the preparation of heterocyclic ring compounds. The aliphatic derivatives have been much less studied. Ruhemann was unable to obtain a tractable[3] substance from the action of allyl mustard oil on malonic ester. Methyl isothiocyanate, however, and its homologs have been observed to form

[1] Original manuscript received July 3, 1931.

[2] Worrall, THIS JOURNAL, **44**, 1551 (1922); **45**, 3092 (1923); **46**, 2832 (1924).

[3] Ruhemann, *J. Chem. Soc.*, **93**, 621 (1908).

crystalline addition[4] products with malonic ester. The resulting esters did not react smoothly with hydroxylamine or hydrazine, substances used in the aromatic series for the preparation of isoxazolones and pyrazolones;[5] moreover, the product contained sulfur in spite of the fact that hydrogen sulfide was evolved in the reaction. Because of these facts and the meager amount of material available, the reaction was not further investigated at the time. In resuming the study of this reaction, allyl mustard oil suggested itself in spite of Ruhemann's discouraging results. The substitution of dimethyl malonate for the usual ethyl ester resulted in a crystalline product, low melting to be sure, but tractable and easily purified. The reaction may be formulated as follows

$$NaCH(COOCH_3)_2 + C_3H_5NCS \longrightarrow CH(COOCH_3)_2C(SNa)NC_3H_5$$

The product was precipitated from water by the addition of hydrochloric acid.

$$CH(COOCH_3)_2C(SNa)NC_3H_5 + HCl = NaCl + CH(COOCH_3)_2C(SH)NC_3H_5$$

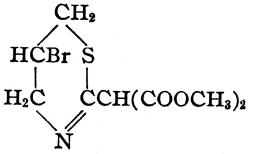
$$CH(COOCH_3)_2C(SH)NC_3H_5 \longrightarrow CH(COOCH_3)_2CSNHC_3H_5$$

The resulting ester was found to react readily with hydrazine. Hydrogen sulfide was evolved and a small amount of a crystalline product was eventually obtained which was identified as malonic acid monothioallylamide. Hydrolysis, not condensation, takes place in the presence of this base. The presence of hydrogen sulfide is due to further decomposition of the new thioamide.

$$CH(COOCH_3)_2CSNHC_3H_5 + 2H_2O \longrightarrow CH_2(COOH)CSNHC_3H_5 + 2CH_3OH + CO_2$$

In this respect the alkyl thioamides differ markedly from the corresponding arylated substances. Bromine was absorbed by the new ester, but the product contained one equivalent only of bromine. It is well known that thioamides, through the enolic form, condense with certain halogenated compounds producing thioazoline bases. Moreover, Dixon[6] has shown that a penthiazoline is formed by the action of bromine on allyl urea. A similar reaction is probable here.

$$CH(COOCH_3)_2C(SH)NCH_2CHBrCH_2Br \longrightarrow HBr +$$



The penthiazoline ester shows only slight evidence of basic character. It readily undergoes hydrolysis when heated with water even without the addition of acid or alkali. Some evidence was found of the presence of hydroxypenthiazoline-acetic acid, but no traces of the intermediate bromo

[4] Worrall, THIS JOURNAL, **50**, 1456 (1928).

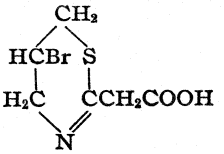
[5] Unpublished results.

[6] Dixon, *J. Chem. Soc.*, **69**, 24 (1896).

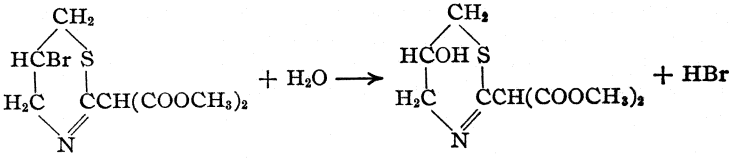
derivative. However, the latter is easily obtained by the action of bromine on malonic acid monothioallylamide.

$$CH_2(COOH)C(SH)NCH_2CH{=}CH_2 + Br_2 \longrightarrow$$

$$CH_2(COOH)C(SH)NCH_2CHBrCH_2Br \longrightarrow HBr +$$



No difficulty was experienced in replacing halogen in the penthiazoline ester with an hydroxyl group without disturbing the ester radical. Alcoholic silver nitrate quickly brought about the desired change.



The product of the action of malonic ester on allyl mustard oil reacts smoothly in the presence of sodium methylate with ethyl chloroacetate, a reaction discovered by Ruhemann, to form a thiophene derivative.

$$CH(COOCH_3)_2C(SNa)NC_3H_5 + CH_2ClCOOC_2H_5 \longrightarrow \underline{C(COOCH_3)_2C(NC_3H_5)SCH_2CO} + NaCl + C_2H_5OH$$

Experimental

Carbomethoxy Methyl Malonate Monothioallylamide.—To 11.5 g. of sodium suspended in 500 cc. of dry ether were added 66 g. of dimethyl malonate and (the next day) 49 g. of allyl mustard oil. The mixture was allowed to stand for some hours with occasional shaking at room temperature, after which it was heated under a reflux condenser for two hours. The entire contents was poured into ice water and the resulting aqueous layer after separation was added slowly with stirring to a freezing mixture of crushed ice and hydrochloric acid. The resulting bulky precipitate was filtered, washed free from chlorides with cold water and then extracted with a rather large volume of a mixture of approximately equal parts of ordinary ethyl alcohol and water warmed merely to room temperature. On cooling to the freezing point of water, a colorless precipitate of flat needle-like crystals quickly appeared. A yield of 77 g. or approximately 66% of the theoretical amount of fairly pure material was obtained in this manner.

Anal. Calcd. for $C_9H_{13}O_4NS$: S, 13.9. Found: S, 13.7.

The pure substance separates from alcohol–water mixtures in the form of brilliant narrow plates melting at 42–43°. It is easily dissolved by the usual organic solvents, also by aqueous sodium hydroxide, from which it may be recovered unchanged in the cold by the prompt addition of dilute acetic acid. The alkaline solution undergoes decomposition on standing at room temperature.

Malonic Acid Monothioallylamide.—Attempts to prepare this substance by the action of alkali on the ester failed. However, by the use of a less vigorous reagent, namely, hydrazine, the above acid was obtained. To 10 g. of the ester dissolved in alcohol was added the molar equivalent of hydrazine. The mixture was then heated under a reflux condenser for four to five hours and allowed to concentrate to a small

volume. The crystalline product separating on the addition of an excess of hydrochloric acid to the dark red solution was recrystallized from water; yield of crude product, approximately two grams.

Anal. Calcd. for $C_6H_9O_2NS \cdot 2H_2O$: S, 16.4. Found: S, 16.4.

It crystallizes from warm water in brilliant plates. The melting point is not sharp, the substance softening at 115° and partially melting with foaming due to the elimination of water at 120–121°. The new thioamide is very soluble in alcohol, although only sparingly soluble in benzene, chloroform and similar solvents.

The preparation of the thiazoline esters may be illustrated by the following experiment. To 30 g. of carbomethoxymethylmalonate monothioallylamide dissolved in a small volume of chloroform and cooled with a freezing mixture was added dropwise the molar equivalent of bromine mixed with chloroform. The clear mixture, after several extractions with cold water to remove hydrobromic acid, was concentrated to a small volume and alcohol added. A prompt removal of the acid is essential as otherwise the substance decomposes even when cold, eventually changing into a tar. The resulting solid after thorough washing with water was crystallized from alcohol; yield of pure material, 27 g.

TABLE I

HALOGEN DERIVATIVES OF PENTHIAZOLINE-2-DIMETHYLMALONATE

	Formula	M. p., °C.	Cryst. form	Halogen, % Calcd.	Found
-5-Chloro	$C_9H_{12}O_4NSCl$	145–146	Microscopic needles	13.4	13.4
-5-Bromo	$C_9H_{12}O_4NSBr$	153–154	Flat needles	25.8	25.6
-5-Iodo	$C_9H_{12}O_4NSI$	156–157	Flat needles	35.6	35.8

A more complete analysis was made of the bromine compound. Calcd. for $C_9H_{12}O_4NSBr$: C, 34.8; H, 3.9; S, 10.3. Found: C, 35.0; H, 4.2; S, 10.3.

These halogen derivatives are sparingly soluble in hot alcohol, but very soluble in chloroform. They are insoluble in cold sodium hydroxide solution or dilute mineral acids and exhibit marked stability toward concentrated nitric acid even after short heating. Permanganate dissolved in acetone is not reduced. Cold concentrated hydrochloric and sulfuric acids dissolve the substances. On heating with water the bromine derivative gradually dissolves. Carbon dioxide is set free, also hydrobromic acid, and a non-tractable gum is formed which gives forth a pyridine-like odor on neutralization with alkali. It is not changed after several hours' heating with methyl iodide and is recovered unchanged after decomposition with water of the addition product with CH_3MgI in ether.

2-Hydroxypenthiazoline-2-dimethylmalonate.—To 5 g. of the bromothiazoline ester dissolved in alcohol was added the molar equivalent of silver nitrate and the mixture heated for several hours. Sodium bicarbonate was then added to neutralize the nitric acid formed in the reaction and the mixture filtered. The filtrate was concentrated to a small bulk from which crystals separated on cooling; yield, 3.5 g. It was recrystallized from alcohol.

Anal. Calcd. for $C_9H_{13}O_5NS \cdot 2H_2O$: S, 11.3. Found: S, 11.3.

The hydroxy derivative is soluble in hot water and readily soluble in hot alcohol, separating in slender flat needles melting at 104–105° with preliminary softening.

While no satisfactory results were obtained in attempts to hydrolyze the above-mentioned esters, it was found possible to obtain the monocarboxyl derivatives by the action of halogens on malonic acid monothioallylamide as follows. To the substance dissolved in glacial acetic acid was added the appropriate amount of the halogen. A prompt precipitation of the halogen acid salt of the carboxyl derivative took place. The

salt was decomposed after filtration by trituration with water mixed with alcohol, following which the penthiazoline was recrystallized from water.

TABLE II

HALOGEN DERIVATIVES OF PENTHIAZOLINE-2-ACETIC ACID

	Formula	M. p., °C.	Cryst. form	Halogen, % Calcd.	Found
-5-Chloro	$C_6H_8O_2NSCl \cdot 2H_2O$	179–180	Powder	15.5	15.3
-5-Bromo	$C_6H_8O_2NSBr \cdot 2H_2O$	188–190	Flat needles	29.2	28.5
-5-Iodo	$C_6H_8O_2NSI \cdot 2H_2O$	213–214	Feathery needles	39.6	39.8

Considerable difficulty was experienced in obtaining satisfactory results with the bromine derivative, for this substance was acted upon by the vapors of fuming nitric acid and apparently bromine was lost before the tube was sealed. After heating, the inside of the Carius tube was spattered with silver bromide. A sulfur determination was made with the following satisfactory results. Calcd. for $C_6H_8O_2NSBr \cdot 2H_2O$: S, 11.7. Found: S, 11.7.

Apparently water of crystallization is lost on standing, for the bromo derivative was observed to change to a crystalline powder.

Anal. Calcd. for $C_6H_8O_2NSBr$: C, 30.5; H, 3.4. Found: C, 30.3; H, 3.5.

These halogen derivatives soften before the melting point is reached and partially decompose with foaming at the melting point. They are very soluble in glacial acetic acid, moderately so in water and insoluble in alcohol, ether, etc. The addition of hydrogen chloride to a glacial acetic acid solution of these substances precipitates the corresponding salt. They are slowly decomposed by hot water, liberating the corresponding halogen acid and forming a gum similar to that obtained by the hydrolysis of the penthiazoline ester.

2-Allylimino-3-dicarbomethoxy-4-ketotetrahydrothiophene.—A solution of 10 g. of carbomethoxy methylmalonate monothioallylamide in methyl alcohol was mixed with the equivalent amount of sodium methylate and ethyl chloroacetate. Considerable heat developed and on standing a dark green color developed. After an hour or so, a small amount of dilute acid was added to decolorize the solution, which was then poured into water. A bulky precipitate of slender lustrous needle-like crystals formed. It was recrystallized from water containing approximately 10% alcohol.

Anal. Calcd. for $C_{11}H_{13}O_5NS$: S, 11.8. Found: S, 11.8.

It is very sparingly soluble in hot water, from which it separates in long snow-white needles melting at 78–79°. On separation from alcohol the substance retains a yellow color which is not removed by repeated crystallization.

Methylcarbomethoxymethylmalonate Monothioallylamide.—Ten grams of methyl dimethylmalonate was condensed in the customary manner with allyl mustard oil and the product shaken with ice water. Then the water extract was slowly run into a freezing mixture of crushed ice and hydrochloric acid. The crude product was recrystallized by shaking with alcohol at room temperature, cooling with ice, and adding a few drops of water. An oil separated out, but on pouring off the turbid liquid and seeding, small colorless crystals resulted. The substance, which melted on warming to room temperature, was not further examined but was allowed to react in chloroform solution cooled to 0° with bromine. Then water was added to extract the hydrobromic acid. However, the solid product quickly changed to a tar on standing. Apparently a penthiazoline was formed, but it subsequently decomposed.

Summary

Allyl mustard oil forms addition products with dimethyl malonate and methyldimethylmalonate.

The first addition product undergoes hydrolysis in the presence of hydrazine into methyl malonate monothioallylamide.

It forms addition products with halogens which through the loss of halogen hydride are immediately converted into penthiazolines.

Carbomethoxymethylmalonate monothioallylamide in the presence of sodium methylate forms a thiophene derivative with ethyl chloroacetate.

TUFTS COLLEGE, MASSACHUSETTS

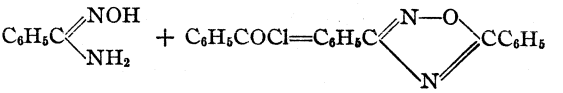
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE FORMATION OF FURO-α,β'-DIAZOLES FROM ACYL IMIDOTHIOCARBONATES AND ACYL PSEUDOTHIOUREAS[1]

BY SHAO TSENG YANG[2] AND TREAT B. JOHNSON

RECEIVED JANUARY 12, 1932 PUBLISHED MAY 7, 1932

A review of the literature of the chemistry of furo-α,β'-diazoles or 1,2,4-oxdiazoles reveals the fact that there are essentially two different methods which are available for the synthesis of representatives of this type of heterocyclic compounds, namely, (1) by interaction of amidoximines with acyl chlorides or acid anhydrides according to Tiemann's well-known reaction expressed below, and which has been extensively studied and applied,[3] and (2) by the action of hydroxylamine on acyl imidothiocar-



bonates and acyl pseudoureas, or reactions which were reported by Johnson and Menge in 1904.[4] This latter method of synthesis has never been carefully studied since its discovery; furthermore, the structures of the resulting diazoles were by no means definitely settled in the original contribution. In this paper we shall describe experimental methods which permit us to decide definitely the constitution of the heterocyclic condensation products obtained by the application of Johnson and Menge's reaction.

Johnson and Menge described one experiment illustrating the behavior of hydroxylamine toward an acyl imidothiocarbonate. They observed that hydroxylamine interacted with diethyl benzoylimidothiocarbonate I at ordinary temperature with formation of a compound to which they as-

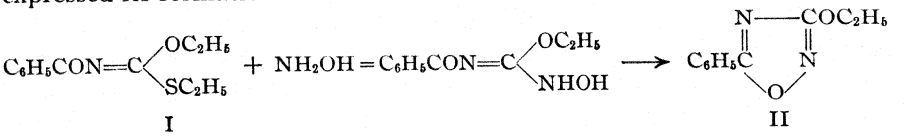
[1] Constructed from a dissertation presented by Shao Tseng Yang to the Faculty of the Graduate School of Yale University, June, 1931, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Holder of a Rockefeller Foundation foreign fellowship, 1929–1931.

[3] Tiemann and Krüger, *Ber.*, **17**, 1685 (1884); and many co-workers between 1884 and 1895.

[4] Johnson and Menge, *Am. Chem. J.*, **32**, 362 (1904).

signed the constitution of α′-phenyl-β-ethoxyfuro-α,β′-diazole II, and expressed its formation as follows

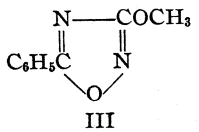


I II

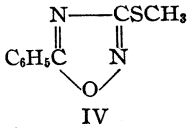
In trying to reproduce the original experiment difficulty was at first encountered in establishing experimental conditions favoring the formation of this furo-α,β′-diazole. Unless a definite technique is applied benzamide is the major product of reaction. The formation of this amide is explained by the fact that the thiocarbonate I is very susceptible to the action of warm alkali and to add hydroxylamine hydrochloride simultaneously with the thiocarbonate I to an alcoholic solution of potassium hydroxide will invariably give benzamide. A free hydroxylamine solution must be first prepared in order to accomplish successfully the desired reaction.

In the second place, the regulation of the temperature when applying the reaction is another very important factor as the change is an exothermic one leading to secondary reactions unless the reaction temperature is kept low. In this respect the dimethyl benzoylimidothiocarbonate is far more sensitive to temperature changes than the diethyl ester I.

The thiocarbonate I and its corresponding dimethyl ester react with hydroxylamine to form the respective furo-α,β′-diazoles represented by formulas II and III. In neither case does hydroxylamine interact with the imidothiocarbonate with formation of a mercaptofuro-α,β′-diazole derivative as represented by formula IV. Furthermore, the two imidothiocarbonates, dimethyl benzoylimidothiocarbonate and O-methyl-S-ethyl benzoylimidothiocarbonate, react with hydroxylamine to give the same furo-α,β′-diazole III. In other words, the mercapto group of the imidothiocarbonate is more readily eliminated by treatment with hydroxylamine than the alkyloxy group. A compound corresponding to formula IV was never detected as a product of this reaction. The formation of such mercapto derivatives of a furo-α,β′-diazole may be predicted by allowing hydroxylamine to interact with acyl imidodithiocarbonates, a reaction which has not hitherto been studied.



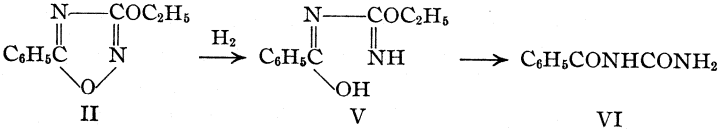
III



IV

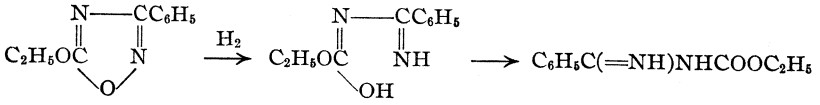
As to the structures of the furo-α,β′-diazoles formed in the above reactions, it was necessary to decide between the two possible isomeric constructions, namely, an α′-phenyl-β-alkoxyl-furo-α,β′-diazole II or α′-

alkoxy-β-phenyl-furo-α,β′-diazole VII. This was accomplished by reduction of our respective furo-α,β′-diazoles with zinc dust and acetic acid. Both of our condensation products II and III were reduced practically quantitatively to benzoylurea VI as is expressed by the equation below. This change involves theoretically the intermediate formation of an acyl-imido ester V. These results confirm the original conclusions of



II V VI

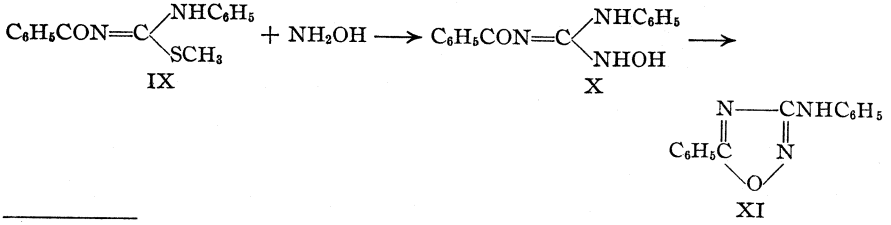
Johnson and Menge. An isomeric α′-alkoxyl-β-phenyl-furo-α,β′-diazole VII would be expected to give by reduction an entirely different product or a urethan derivative of benzamidine VIII as is illustrated by the equation



VII VIII

The behavior of our furo-α,β′-diazoles on reduction is entirely in accord with that of the anhydroximes on reduction, which were investigated by Rose and Scott.[5] This method of establishing structure is undoubtedly applicable to other heterocyclic constructions containing the furo-α,β′-diazole ring.

α′-Phenyl-β-anilino-furo-α,β′-diazole XI is formed by the action of hydroxylamine on benzoylpseudomethylphenylthiourea in pyridine solution.[6] Johnson and Menge state in their original paper that this type of transformation is accomplished by interaction of hydroxylamine with an acylimidopseudourea, but no experimental evidence in support of this was presented. It has been our experience that the oxygen pseudoureas are not as reactive toward hydroxylamine as the corresponding sulfur analogs; therefore, we confined our work to the study of the sulfur derivatives. The reaction leading to the formation of an anilino-furo-α,β′-diazole is given below

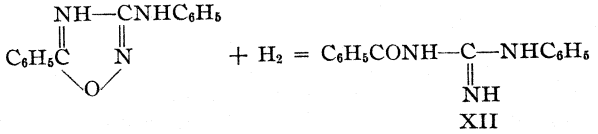


IX X XI

[5] Rose and Scott, THIS JOURNAL, **39**, 273 (1917).

[6] Wheeler and Merriam, *ibid.*, **23**, 293 (1901).

The pseudothiourea IX used in this work, which was first prepared by Wheeler and Merriam[6] by the action of aniline on dimethyl benzoylimidodithiocarbonate, was synthesized by the direct alkylation of *sym.*-benzoylphenylthiourea with methyl iodide. When the furo-α,β'-diazole XI was reduced with zinc and acetic acid it was converted smoothly into benzoylphenylguanidine XII, a change which establishes its constitution. The



free guanidine melted at 90–91°, and the picrate of the guanidine melted at 187–188°. These results, therefore, identify the reduction product as the guanidine derivative previously described by Wheeler and Johnson.[7] In other words, the acyl imidothiocarbonates and the corresponding pseudothioureas interact with hydroxylamine in a similar manner with evolution of mercaptan and formation of well characterized, crystalline furo-α,β'-diazole compounds.

Experimental Part

Preparation of Acylimidothiocarbonates.—Dimethyl benzoylimidothiocarbonate, $C_6H_5CON{=}C(OCH_3)SCH_3$,[8] was prepared by alkylation of methyl benzoylthioncarbonate[9] in alkaline solution with methyl iodide. It melted at 46° after recrystallization from ether. The corresponding diethyl imidothiocarbonate was prepared in an analogous manner by alkylation of ethyl benzoylthiocarbamate with ethyl bromide. It boiled at 200–203° at 16 mm. (Wheeler and Johnson reported the temperature of 209–212° at 19 mm.). The mixed ester O-methyl-S-ethyl benzoylimidothiocarbonate, which was prepared by the action of ethyl bromide on the potassium salt of methyl benzoylthioncarbamate, boiled at 195–205° at 14 mm.

Preparation of Acyl Pseudothioureas.—The pseudomethyl benzoylphenylthiourea, $C_6H_5CON{=}C(SCH_3)NHC_6H_5$, and the corresponding pseudoethyl compound used in this work were prepared by the direct alkylation of *sym.*-benzoylphenylthiourea in sodium alcoholate solution with methyl iodide and ethyl bromide, respectively. The pseudomethyl compound was obtained in a yield of 70% and melted at 104–105°,[10] and the pseudoethyl compound melted at the temperature of 88°, as originally reported by Wheeler and Merriam.

α'-Phenyl-β-methoxy-furo-α,β'-diazole, $C_9H_8O_2N_2$ (III).—This compound is easily prepared as follows: 56 g. of dimethyl benzoylimidothiocarbonate is dissolved in 50 cc. of 95% alcohol and the solution combined with an alcoholic solution of hydroxylamine, prepared by adding 19 g. of hydroxylamine hydrochloride to a solution of 15 g. of potassium hydroxide in 100 cc. of methyl alcohol. The solutions were mixed at a low

[7] Wheeler and Johnson, *Am. Chem. J.*, **26**, 417 (1901).

[8] Wheeler and Johnson, *ibid.*, **24**, 200 (1900); Johnson and Menge, *ibid.*, **32**, 364 (1904).

[9] Miquel, *Ann. chim.*, [5] **11**, 330 (1877). Wheeler and Johnson, *Am. Chem. J.*, **24**, 200 (1900).

[10] See Wheeler and Merriam, THIS JOURNAL, **23**, 290 (1901).

temperature and then allowed to stand in an ice chest for forty-eight hours. The alcohol solution was then poured into cold water when the furo-α,β'-diazole separated as an oil which soon solidified. It was purified by crystallization from dilute alcohol and separated in the form of prisms. Some of these crystals were more than one inch in length. The yield of purified furo-α,β'-diazole was 31 g. It melted at 58–59°.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.36; H, 4.54; N, 15.90. Found: C, 61.28; H, 4.60; N, 16.05.

The furo-α,β'-diazole is insoluble in water, moderately so in ligroin and very soluble in alcohol, ethyl acetate, chloroform, ether and benzene.

α'-Phenyl-β-ethoxy-furo-α,β'-diazole, $C_{10}H_{10}O_2N_2$ (II).—This furo-α,β'-diazole was prepared according to the same technique described in the previous experiment by allowing hydroxylamine to interact with diethyl benzoylimidothiocarbonate at ordinary temperature. After standing in an ice chest for thirty-six hours, the alcohol solution was poured into water, when the furo-α,β'-diazole separated as an oil which solidified almost immediately. It was purified by recrystallization from 95% alcohol and separated in the form of stout prisms melting at 49–50°. The solubility of this compound is similar to that of the corresponding methoxy compound.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: N, 14.73. Found: N, 14.83.

These two furo-α,β'-diazoles are characterized by their great stability and extreme inertness. Notwithstanding the fact that they contain an imido ester grouping they do not form salts with the acids—hydrochloric, nitric and sulfuric. In concentrated hydrochloric acid they remain undissolved in the cold and on warming the acid the furo-α,β'-diazoles melt without alteration. In concentrated sulfuric and nitric acids both furo-α,β'-diazoles dissolve in the cold and are reprecipitated unchanged by dilution of the acid solutions with water. They are not attacked by concentrated nitric acid when the acid solution is heated at the boiling point for several minutes. They can be heated to 250° without decomposition. They do not react with aniline at its boiling point, and can be heated with alcoholic ammonia at 200–250° for hours without alteration. We obtained no evidence that Wieland and Bauer's[11] α'-phenyl-β-amino-furo-α,β'-diazole is formed by interaction with ammonia. Neither of the two furo-α,β'-diazoles responds favorably to the experimental conditions employed in applying a Zeisel reaction. The furodiazole nucleus is completely destroyed by hydriodic acid at 100° with the formation of benzoic acid.

Reduction of α'-Phenyl-β-methoxy-furo-α,β'-diazole with Zinc and Glacial Acetic Acid.—Five grams of this furo-α,β'-diazole was dissolved in 25 cc. of cold glacial acetic acid and ten grams of zinc dust added. The mixture was then heated at 85–90° for one hour and finally allowed to stand for three hours, when the unchanged zinc was removed by filtration and the excess of acetic acid evaporated on a water-bath. A crystalline residue was obtained. This was identified as a mixture of the unaltered furo-α,β'-diazole and benzoylurea. About one-half of the furo-α,β'-diazole was recovered unchanged. On recrystallizing the crude reduction product from alcohol the urea was obtained in pure form melting at 208°.

Anal. Calcd. for $C_8H_8O_2N_2$: N, 17.07. Found: N, 17.00.

When the corresponding α'-phenyl-β-ethoxy-furo-α,β'-diazole was reduced with zinc dust and acetic acid under the same conditions it was also converted into benzoylurea. After digesting with zinc at 95–100° for three hours, about one-half of the furo-α,β'-diazole was still recovered unaltered.

α-Phenyl-β-anilino-furo-α,β'-diazole, $C_{14}H_{11}ON_3$ (XI).—This furo-α,β'-diazole is

[11] Wieland and Bauer, *Ber.*, **40**, 1691 (1907).

formed by the action of hydroxylamine on pseudomethyl benzoylphenylthiourea or pseudoethyl benzoylphenylthiourea. One experiment will be described in order to illustrate the technique employed. Ten grams of pseudomethyl benzoylphenylthiourea was dissolved in 25 cc. of pyridine and two molecular proportions of hydroxylamine hydrochloride added to the solution while cooling. After allowing to stand for about forty-eight hours the pyridine solution was diluted with water, when the above furo-α,β'-diazole separated in a crystalline condition. This crude reaction product was washed with dilute sulfuric acid to remove traces of pyridine and then recrystallized from benzene. It separated, on cooling, in the form of rectangular prisms melting at 139–140°. It did not respond to a test for sulfur and also crystallized from alcohol in prisms melting at 139–140°. For analysis the compound was dried at 110–120° to constant weight.

Anal. Calcd. for N, 17.72. Found: N, 17.62, 17.70.

The furo-α,β'-diazole did not interact with acetic anhydride by refluxing with this reagent for three hours. It dissolved in concentrated sulfuric acid in the cold, giving a red colored solution. On diluting the acid solution with water the furo-α,β'-diazole was precipitated unchanged.

Behavior on Reduction.—Two grams of the anilino-furo-α,β'-diazole was reduced with zinc dust and glacial acetic acid at 90–95° for three hours. After removing the excess of zinc and evaporating the acetic acid, a crystalline substance was obtained which was purified by crystallization from benzene. It was identified as benzoylphenylguanidine and melted at 90–91°. When picric acid was added to an alcoholic solution of the base, the picrate separated as reported previously by Wheeler and Johnson.[7]

Anal. (Picrate). Calcd. for $C_{20}H_{16}O_8N_6$: N, 17.94. Found: N, 17.80.

β-Chlorethyl Benzoylthioncarbamate, $C_6H_5CONHCSOCH_2CH_2Cl$.—This compound is easily prepared by allowing freshly distilled benzoyl isothiocyanate to interact at ordinary temperature with ethylene chlorohydrin. The thioncarbamate was purified by crystallization from acetone or alcohol and crystallized in the form of needles melting at 179–180°.

Anal. Calcd. for $C_{10}H_{10}O_2NSCl$: N, 5.71. Found: N, 5.74, 5.83.

Summary

1. Acylimidothiocarbonates react with hydroxylamine to form alkoxyl furo-α,β'-diazoles.

2. Pseudoalkylacylphenylthioureas react with hydroxylamine to form anilino-furo-α,β'-diazoles.

3. The structures of heterocyclic combinations of the furo-α,β'-diazole type are established by their behavior on reduction with zinc and acetic acid. The alkoxyl compounds are broken down with formation of acylureas while the anilino derivatives give acyl derivatives of substituted guanidines.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORMATION OF 1,4-DIPHENYLHEXADIENE-1,5 IN THE REACTION BETWEEN CINNAMYL CHLORIDE AND MAGNESIUM

BY HENRY GILMAN AND STANTON A. HARRIS

RECEIVED JANUARY 12, 1932 PUBLISHED MAY 7, 1932

Introduction

Two hydrocarbons have been isolated in the unusual reaction between cinnamyl chloride and magnesium.[1] One of these has been identified definitely as the solid dicinnamyl, $C_6H_5CH{=}CHCH_2CH_2CH{=}CHC_6H_5$. The other hydrocarbon, a liquid, has been designated as 1,4-diphenylhexene-1 and is said to owe its origin to the following reactions

$$\begin{array}{l} C_6H_5CH{=}CHCH_2MgCl \\ + \\ C_6H_5CH{=}CHCH_2MgCl \end{array} \longrightarrow C_6H_5CH(MgCl)CH_2MgCl \xrightarrow{(HOH)} \begin{array}{l} C_6H_5CHCH_2CH_3 \\ | \\ CH_2CH{=}CHC_6H_5 \\ (A) \end{array} \quad (I)$$

That is, Compound (A) is formed as a consequence of the addition of one molecule of the so-called cinnamylmagnesium chloride to the ethylenic linkage of another molecule of this Grignard reagent. The evidence in support of (A) turns on its ultimate analysis and its oxidation to phenylsuccinic and benzoic acids.

It has also been suggested[2] that the liquid hydrocarbon might be a diolefin formed as follows

$$\begin{array}{l} C_6H_5CH{=}CHCH_2MgCl \\ + \\ C_6H_5CH{=}CHCH_2Cl \end{array} \longrightarrow C_6H_5CH(MgCl)CH_2Cl \xrightarrow{-MgCl_2} \begin{array}{l} C_6H_5CHCH{=}CH_2 \\ | \\ CH_2CH{=}CHC_6H_5 \\ (B) \end{array} \quad (II)$$

In this mechanism, one molecule of the RMgCl compound adds to the ethylenic linkage of a molecule of cinnamyl chloride to give a new Grignard reagent which then loses magnesium chloride.

Each of these mechanisms suffers from the disadvantage that it postulates addition of a Grignard reagent to an ethylenic linkage. No such addition has been established, and present evidence is overwhelmingly against it.[3] We have shown that the liquid hydrocarbon is Compound

[1] Rupe and Bürgin, *Ber.*, **43**, 172 (1910).

[2] V. Braun and Köhler, *ibid.*, **51**, 79 (1918).

[3] A recent article with leading references on the non-addition of RMgX compounds to an ethylenic linkage is Gilman and Harris, *Rec. trav. chim.*, **49**, 762 (1930). It should be stated that the postulation of such addition was made at a time when there appeared

(B), 1,4-diphenylhexadiene-1,5. This was demonstrated: first, by ultimate analysis, the values for carbon and hydrogen agreeing better for Compound (B) than for (A); second, by catalytic reduction whereby exactly two moles of hydrogen were taken up; third, by ozonization that gave formaldehyde and benzaldehyde, which together with the phenylsuccinic acid obtained previously[1] by permanganate oxidation, definitely supports (B) and makes (A) altogether unlikely because it would hardly be expected to give any formaldehyde, and phenylsuccinic acid is rather to be expected with (B) than (A); and, fourth, by definitely establishing the identity of the reduction product with an authentic specimen of 1,4-diphenylhexane.

The evidence based on reduction to 1,4-diphenylhexane obviously supports both (A) and (B). It has been presented, however, in order to exclude a third possible compound, namely, 3,4-diphenylhexadiene-1,5.

$$\begin{array}{l} C_6H_5CH{-}CH{=}CH_2 \\ \quad\quad | \\ C_6H_5CH{-}CH{=}CH_2 \end{array} \qquad (C)$$

Actually, Compound (C) has been suggested[4] tentatively as a structure for the oil obtained in related reactions between cinnamyl bromide and ethylmagnesium bromide and phenylmagnesium bromide, respectively. Were it not for the facts that Compound (C) does not agree with the reduction and oxidation products of the liquid hydrocarbon, it might be considered a possibility for the following reasons.

First, it appears altogether probable that the first step involved in a reaction between an RX compound and magnesium in ether is the formation of a free radical which can undergo several reactions, among which are coupling to give an R·R compound, rearrangement to a different free radical and disproportionation.[5] Second, the R·R compound can be formed as follows, also through the intermediate free radicals.[5]

$$2\,RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + MgX_2 \qquad (III)$$

$$RX + RMgX \longrightarrow R{\cdot}R + MgX_2 \qquad (IV)$$

Third, the reaction between cinnamyl chloride and magnesium gives a

to be some basis for such reaction, and that Professor Rupe is now of the opinion that a Grignard reagent does not add to an ethylenic linkage. See, in this connection, Gilman and Schulz, THIS JOURNAL, **53**, 2799 (1931).

[4] Prévost and Danjat, *Bull. soc. chim.*, **47**, 588 (1930). See, also, Kirrmann, *ibid.*, **47**, 834 (1930). V. Braun and Köhler, *Ber.*, **51**, 83 (1918), earlier studied the reaction between cinnamyl bromide and ethyl- and phenylmagnesium halides.

In a paper by Prévost, *Bull. soc. chim.* **49**, 1372 (1931) [*C. A.* **26**, 1574 (1932)], which became available after our manuscript was submitted for publication, it has been shown that the second hydrocarbon is 1,4-diphenylhexadiene-1,5.

[5] A recent article with leading references is Gilman and Zoellner, THIS JOURNAL, **52**, 3984 (1930).

Grignard reagent which reacts[6] with a wide variety of compounds as though its formula were $C_6H_5CHCH{=}CH_2$ (with MgCl) and not $C_6H_5CH{=}CHCH_2MgCl$.

For these reasons, the two radicals expected in a reaction between cinnamyl chloride and magnesium are

$$C_6H_5CH{=}CHCH_2{-} \text{ and } C_6H_5CHCH{=}CH_2$$

The union of two of the former (cinnamyl) radicals would give dicinnamyl; the union of two of the latter (α-phenylallyl) radicals would give Compound (C), 3,4-diphenylhexadiene-1,5; and the union of one of each of these radicals would give Compound (B), 1,4-diphenylhexadiene-1,5.

We thus see that there is no basis of expectation, on theoretical grounds, for Compound (A), 1,4-diphenylhexene-1. Compound (C) may be contained in the oily mixture of hydrocarbons which has so far definitely yielded dicinnamyl and 1,4-diphenylhexadiene-1,5 (B). The proportions of R·R compounds in such reactions varies with experimental conditions and with the nature of halogen in the RX compound. For example, with cinnamyl bromide and magnesium the chief hydrocarbon is dicinnamyl[2] and not, as with cinnamyl chloride, 1,4-diphenylhexadiene-1,5.

Experimental Part

Preparation of Hydrocarbon Mixture.—In a typical experiment, 60.8 g. (0.4 mole) of cinnamyl chloride (melting at 7–8°) dissolved in 100 cc. of ether, was added to 5 g. (0.205 atom) of magnesium, the reaction being first started with a small quantity of ether. At the end of the reaction, there was a slight positive color test[7] showing the presence of a small quantity of Grignard reagent.[8] This was destroyed by the addition of 2 cc. of cinnamyl chloride. The solution was then hydrolyzed, and the ether layer dried over calcium chloride and then distilled. On the first distillation, a total yield of 34.9 g. or 74.5% of hydrocarbons was obtained, boiling over the range 165–180° (3–4 mm.). The last portion of the distillate crystallized in the receiver, and was identified as dicinnamyl. After five fractionations, 20 g. or a 42.9% yield of hydrocarbon, distilling at 157–160° (2 mm.), was obtained: n_D^{20} 1.5890; d_{20}^{20} 0.9919. The higher fraction yielded 4.1 g. or 8.75% of dicinnamyl. An intermediate fraction was not investigated.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.95.

Catalytic Reduction of Liquid Hydrocarbon.—The reduction of 11.7 g. (0.05 mole) of hydrocarbon in 50 cc. of alcohol was effected with 0.15 g. of Adams' catalyst. In ten minutes, 7.6 pounds (0.1 mole) of hydrogen was absorbed, showing the presence of two ethylenic linkages. Like results were obtained with 0.025 mole of the hydrocarbon.

---

[6] Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927); *ibid.*, **53**, 3541 (1931). This latter reference and that of Gilman and Kirby, *ibid.*, **54**, 345 (1932), describe several mechanisms proposed for the allylic rearrangements of Grignard reagents like cinnamylmagnesium chloride. See, also, Austin and Johnson, *ibid.*, **54**, 647 (1932).

[7] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[8] Cinnamylmagnesium chloride can be prepared in an 87% yield. See Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

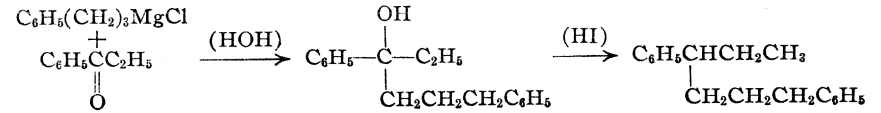
The product, subsequently identified as 1,4-diphenylhexane, boiled at 147–148° (3 mm.); n_D^{20} 1.5456; d_{20}^{20} 0.9608.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.75; H, 9.24. Found: C, 90.4; H, 9.16.

Dicinnamyl likewise took up the theoretical quantity of hydrogen.

Ozonization of Liquid Hydrocarbon.—Ozonization, by the procedure of Doeuvre,[9] gave formaldehyde and benzaldehyde. Under the same conditions, dicinnamyl yielded benzaldehyde but no formaldehyde.

Synthesis of 1,4-Diphenylhexane.—The following transformations were used in the preparation of 1,4-diphenylhexane.



The γ-phenylpropyl chloride was obtained in an 82% yield by heating an ether solution of 80 g. (0.59 mole) of γ-phenylpropyl alcohol with 75 g. (0.63 mole) of thionyl chloride for one hour. The corresponding Grignard reagent, γ-phenylpropylmagnesium chloride, was obtained in a 98% yield[10] in a 0.5 mole run, the reaction being started with activated magnesium–copper alloy. When treated in a customary manner with propiophenone, the Grignard product yielded 81.5 g. or a 64% yield of 1,4-diphenylhexanol-4; b. p. 177–179°; n_D^{20} 1.5508; d_{20}^{20} 1.0284.

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 84.96; H, 8.69.

Twelve and one-half grams of the carbinol was heated in a pressure bottle with 25 cc. of constant boiling hydriodic acid and some red phosphorus for two hours at 140–150°. The synthetic 1,4-diphenylhexane obtained in this manner had the following constants: b. p. 147–149° (3–4 mm.); n_D^{20} 1.5460; d_{20}^{20} 9660.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.75; H, 9.24. Found: C, 90.57; H, 9.19.

Summary

The liquid hydrocarbon formed from cinnamyl chloride and magnesium in ether has been shown to be 1,4-diphenylhexadiene-1,5 and not 1,4-diphenylhexene-1, as previously reported. Mechanisms have been proposed for its formation.

AMES, IOWA

[9] Doeuvre, *Bull. soc. chim.*, **45**, 140 (1929).

[10] By the acid-titration method of Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923). See, also, Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929).

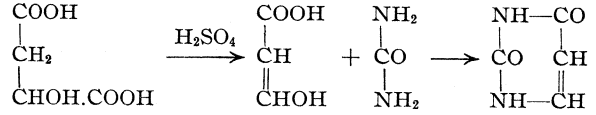
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE FERTILIZER AND FIXED NITROGEN DIVISION OF THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

PREPARATIONS OF URACIL-4-ACETIC AND OROTIC ACIDS. OROTIC ACID AS THE POSSIBLE INTERMEDIATE IN THE SYNTHESIS OF PURINES FROM HISTIDINE

BY GUIDO E. HILBERT

RECEIVED JANUARY 22, 1932 PUBLISHED MAY 7, 1932

The excellent method of Davidson and Baudisch[1] for the synthesis of uracil consists in treating malic acid and urea with fuming sulfuric acid.



This synthesis is of considerable significance since it allows an easy mode of entrance into the pyrimidine series of compounds. With uracil as a starting material, many pyrimidines substituted in the 1, 2, 3, 5 and 6 positions can easily be made. Hilbert and Johnson[2] have taken advantage of this procedure and synthesized cytosine by a new method. More recently[3] it has been demonstrated that thymine can also be prepared directly from uracil in a manner analogous to Kircher's[4] synthesis of 4,5-dimethyluracil from 4-methyluracil. The reaction was carried out by treating uracil with formaldehyde and hydrochloric acid. The resulting uracil-5-methyl chloride was reduced with tin and hydrochloric acid and yielded thymine. Since the method of Davidson and Baudisch for the preparation of uracil is far superior to the older one of Wheeler and Merriam,[5] it was of interest to determine if it could also be applied for the preparation of other pyrimidines.

The Syntheses of Uracil-4-Acetic and Orotic Acids.—It is reasonable to expect that other α-hydroxy-α,β-dicarboxylic acids will also break down with fuming sulfuric acid in a manner typical of α-hydroxy acids to yield products which will combine with urea to form cyclic ureides. The easily available citric acid has such a configuration and should yield, with urea, uracil-4-acetic acid, a view which has now been confirmed.

As is well known, citric acid in the presence of fuming sulfuric acid breaks down to form acetonedicarboxylic acid. It was either this or more probably the enol form which condensed with the urea to form uracil-4-acetic acid. The structure of the pyrimidine was proved beyond reasonable

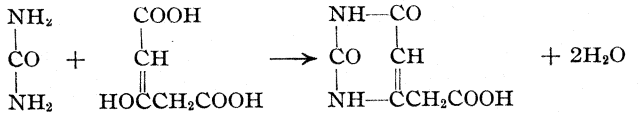
[1] Davidson and Baudisch, THIS JOURNAL, **48**, 2379 (1926).

[2] Hilbert and Johnson, *ibid.*, **52**, 1152 (1930).

[3] Unpublished results.

[4] Kircher, *Ann.*, **385**, 293 (1911).

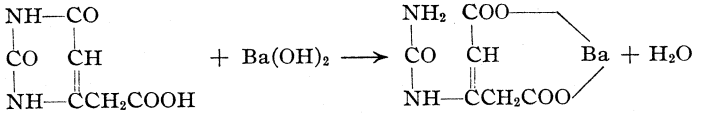
[5] Wheeler and Merriam, *Am. Chem. J.*, **29**, 478 (1903).



doubt since the properties of it and a number of derivatives were the same as those recorded by Wheeler and Liddle.[6] The method is recommended the best for the preparation of this substance.

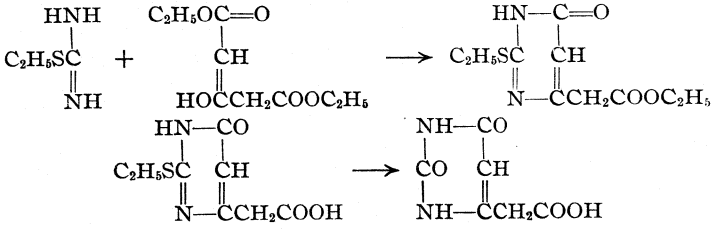
The limitations of this method for the synthesis of pyrimidines are well illustrated by the failure to isolate any products when ethyl acetoacetate and ethyl sodiumformylpropionate were used (for other examples see experimental portion) in place of malic or citric acids. Theoretically, one would have expected the synthesis of 4-methyluracil and thymine, respectively. The fact that these latter experiments were unsuccessful seems surprising, since these compounds are so similar in structure to formylacetic and acetonedicarboxylic acids which react so smoothly.

The attempt to decarboxylate uracil-4-acetic acid by treatment with barium hydroxide solution was unsuccessful, since the pyrimidine ring was ruptured, yielding the insoluble barium salt of β-carbamidoglutaconic acid. This was readily decomposed by hydrochloric acid and regenerated uracil-4-acetic acid, indicating that the salt probably was the *cis*[7] modification. Although the rupture of a pyrimidine having a double bond in the 4,5 posi-



tion was odd, it was not new. Müller[8] condensed ethyl oxaloacetate with methylurea and obtained 3-methyluracil-4-ethylcarboxylate. When the sodium salt of this substance was treated with hydrochloric acid a β-methylcarbamidoacrylic acid, $-H_2NCON(CH_3)CH=CHCOOH$, was obtained. Neither acids nor alkali converted this substance into 3-methyluracil.

[6] Wheeler and Liddle [THIS JOURNAL, **30**, 1156 (1908)] previously synthesized uracil-4-acetic acid. Acetonediethylcarboxylate was condensed with 2-ethylpseudothiourea in alkaline solution and yielded 2-ethylmercapto-6-oxypyrimidine-4-ethylacetate. This was saponified and the resulting mercapto acid digested with concentrated hydrochloric acid to form uracil-4-acetic acid.



[7] *Cis* with respect to the newly formed carboxyl and ureido groups.

[8] Müller, *J. prakt. Chem.*, **56**, 498 (1897).

Johnson and Shepard[9] have reported a similar case. They isolated a by-product in the reaction of 2-thiouracil with sodium ethylate and ethyl chloroacetate which they believed to be β-thiocarbamidoacrylic acid, that was unaffected by acids. The fact that these acrylic acid derivatives did not yield pyrimidines on acid treatment was interpreted as indicating that they had the *trans* configuration.[10]

In order to obtain further information on the ease of hydrogenation of the 4,5 double bond in keto pyrimidines, uracil-4-ethylacetate and 3-methyluracil were hydrogenated using Adams and Shriner's platinum oxide as catalyst. The saturation of the double bond in both cases was found to be very slow.

Biscaro and Belloni[11] in 1905 isolated orotic acid from milk. Recently Bachstez[12] showed that it was identical with uracil-4-carboxylic acid, which has been synthesized a number of times. Müller[13] prepared the ethyl ester by condensing urea with ethyl oxaloacetate in acetic acid. This was subsequently saponified to the acid by Wheeler.[14]

Later Behrend and Struve[15] synthesized the acid by the oxidation of 4-methyluracil in potassium hydroxide solution with potassium ferricyanide. More recently Johnson and Schroeder[16] have prepared it by the oxidation of uracil-4-aldehyde with chromic acid. Of these methods, that of Behrend and Struve appears to be the best since 4-methyluracil is readily available and the oxidation can easily be carried out, resulting in a good yield of orotic acid. As uracil-4-acetic acid can now be made as easily as 4-methyluracil, its smooth oxidation would be expected to lead to another convenient synthesis of orotic acid. The action of potassium ferricyanide on uracil-4-acetic acid in alkaline solution was studied. The oxidation did not go as smoothly as that of 4-methyluracil; the yield of orotic acid was somewhat less. It is possible that the ease in rupture of the ring was partly responsible for the decreased yield. Under the conditions operated, the method, as yet, cannot be recommended as being better than that of the oxidation of 4-methyl-uracil.

[9] Johnson and Shepard, *Am. Chem. J.*, **46**, 345 (1911).

[10] A number of examples have been reported in which the acrylic acid derivative was converted to a pyrimidine by treatment with acid. Behrend, *Ann.*, **229**, 8 (1885), noted that a carbamidocrotonic ester was converted to 4-methyluracil and Johnson and Clapp [*Am. Chem. J.*, **32**, 130 (1904)] found that α-methyl-β-guanidinoacrylic acid was changed to 2-amino-5-methyl-6-oxypyrimidine. In these cases the acid was assigned the *cis* structure.

[11] Biscaro and Belloni, *Estratto Annuario Soc. Chimica di Milano*, **11**, 1 (1905); *Chem. Centr.*, II, 63 (1905).

[12] Bachstez, *Ber.*, **63**, 1000 (1930); *Giorn. chim. ind. applicata*, **12**, 174 (1930).

[13] Müller, *J. prakt. Chem.*, **56**, 488 (1897).

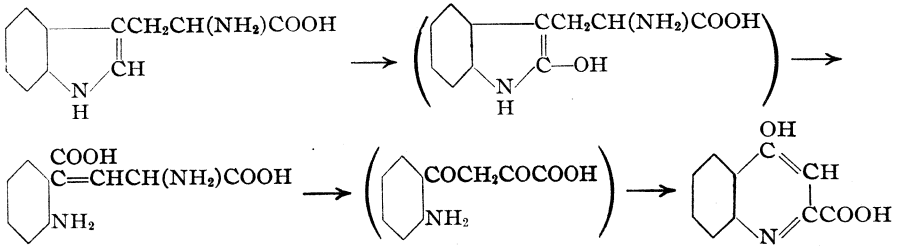
[14] Wheeler, *Am. Chem. J.*, **38**, 358 (1907).

[15] Behrend and Struve, *Ann.*, **378**, 153 (1910).

[16] Johnson and Schroeder, THIS JOURNAL, **53**, 1989 (1931).

Orotic Acid as the Possible Intermediate in the Synthesis of Purines from Histidine.—The occurrence of orotic acid in milk arouses interest as to the possible mechanism of its formation and the role that it may play in metabolism.[17] Because of the carbon grouping in position 4 it seems improbable that it is a degradation product of either purines or the pyrimidine nucleosides. The possibility that uracil might be the precursor of orotic acid is also unattractive. The conversion of uracil into orotic acid requires considerable energy as, in general, decarboxylations involve a decrease in free energy. One might thus expect that the synthesis of this product at the expense of considerable energy would necessitate its playing a rather important role in the organism regarding which, as yet, there is a lack of any positive information. A more plausible explanation is that which is suggested by the relationship of kynurenic acid to tryptophane.

Kynurenic acid (II) was first isolated from the urine of dogs by Liebig. Ellinger[18] in 1904 definitely proved that it was a metabolic product of tryptophane. A number of mechanisms[19] for the formation of kynurenic acid have been suggested; however, that proposed by Kotake and co-workers[20] is the most probable one. They have been able to isolate an intermediate—kynurenine (1)—that was converted either by an organism or barium hydroxide solution to kynurenic acid. They have offered the following scheme for the conversion of tryptophane to kynurenic acid.



I II

An inspection of the structures of tryptophane and histidine shows that they have in common the grouping $\begin{array}{l} \text{—CCH}_2\text{CH(NH}_2\text{)COOH} \\ \quad\quad\quad\quad\quad\quad\quad\quad \| \\ \text{—NH—CH} \end{array}$ which, in the case of tryptophane, is directly involved in the conversion of the indole

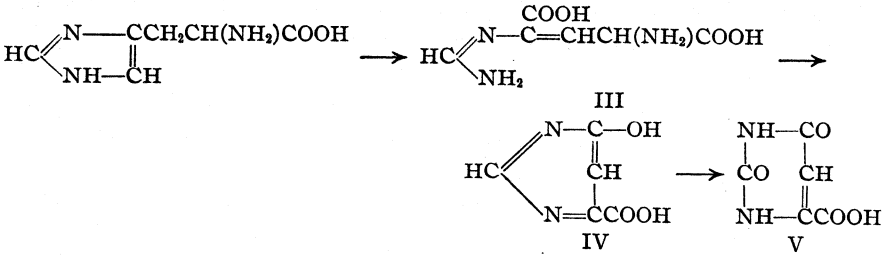
[17] It is possible that the orotic acid comes directly from the diet, that is, it might be a plant product. It has not as yet, however, been shown to occur in plants.

[18] Ellinger, *Z. physiol. Chem.*, **43**, 325 (1904).

[19] Ellinger and Matsuoka, *ibid.*, **109**, 259 (1920); Robson, *Biochem. J.*, **22**, 1157 (1928).

[20] Kotake and Iwao, *Z. physiol. Chem.*, **195**, 139 (1931); Kotake and Kiyokawa, *ibid.*, **195**, 147 (1931); Kotake and Shichiri, *ibid.*, **195**, 152 (1931); Kotake, *ibid.*, **195**, 158 (1931); Kotake and Ichihara, *ibid.*, **195**, 171 (1931); Shichiri and Kiyokawa, *ibid.*, **195**, 166 (1931).

to the quinoline compound. The postulation of an analogous transformation with histidine results in the formation of a pyrimidine ring.



The intermediate (III) is the analog of kynurenine and (IV) of kynurenic acid. An additional oxidation of the 2 position of either the imidazole or the pyrimidine yields the 2-oxypyrimidine–orotic acid (V). That such an oxidation is possible is indicated by the well-known conversion of purines in the organism to uric acid.

This set of equations represents not only the idea that histidine is the precursor of orotic acid but also suggests a mechanism of purine synthesis from histidine. The ease with which purines can be synthesized from pyrimidines *in vitro* has led a number of investigators to suggest that the latter may be the precursors of the former. The conversion of orotic acid to purines is quite easy to picture, since every step but one has already been reported in the literature. The decarboxylation of orotic acid yields uracil. This was converted by Wheeler and Johnson[21] into isodialuric acid, with which, upon heating with urea, Behrend and Roosen[22] synthesized uric acid.

In addition to the striking analogy that it bears to the intermediary metabolism of tryptophane, the above speculations are supported by the work of Ackroyd and Hopkins,[23] Rose and Cook,[24] and Stewart.[25] In general they found that in the absence of histidine in the diet, the allantoin content of the urine decreased. As allantoin is usually accounted for by the oxidation of uric acid, they interpreted this as indicating that histidine was the precursor of the purines, and hence essential for nuclear synthesis. A number of other investigators, however, have reported negative results. Mitchell and Hamilton[26] aptly summarized the status of the work in the following quotation, "Many negative results have been reported from experiments designed to establish a relationship between

[21] Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).

[22] Behrend and Roosen, *Ann.*, **251**, 235 (1888).

[23] Ackroyd and Hopkins, *Biochem. J.*, **10**, 551 (1916).

[24] Rose and Cook, *J. Biol. Chem.*, **64**, 325 (1925).

[25] Stewart, *Biochem. J.*, **19**, 1101 (1925).

[26] Mitchell and Hamilton, "The Biochemistry of the Amino Acids," New York, 1929, p. 360.

histidine and purines in animal metabolism but such results cannot be considered as invalidating the positive indications that have been observed."

In the absence of any experimental work on a relation between histidine and orotic acid, it must be emphasized that the above discussion is of a speculative nature but has been offered as it might prove of value in the elucidation of the intermediary metabolism of histidine and the anabolism of pyrimidines and purines.

I am greatly indebted to Dr. Reid T. Milner and Mrs. Mildred Sherman for carrying out the microanalyses recorded in this paper.

Experimental

In the course of various investigations on pyrimidines large quantities of uracil were required, so attempts were made to improve upon the method of Davidson and Baudisch. The modification consisted of reversing the procedure of Davidson and Baudisch with regard to the addition of urea and malic acid to fuming sulfuric acid, and heating to 85°. This was an improvement inasmuch as it cut down to one-half the time devoted to the experiment and also increased the yield by 20%.

Uracil-4-acetic Acid.—A large number of experiments was carried out under different experimental conditions. The success of the experiment was dependent upon the amount of sulfur trioxide in the fuming sulfuric acid and the temperature to which the reaction mixture was heated. Much variation of these two factors decreased the yield enormously. The following procedure was found to give the best results. To a 3-liter three-necked flask equipped with a stirrer was added 400 cc. of fuming sulfuric acid containing 15% sulfur trioxide. The acid was cooled to −10° and 80 g. of finely ground citric acid added at such a rate that the temperature did not rise above 5°; this usually required about fifteen minutes. If the temperature rose to 10°, an appreciable amount of the acetone dicarboxylic acid was formed. Since this reaction took place with the evolution of heat, considerable trouble was experienced in attempting to lower the temperature. The remainder of the citric acid, 80 g., and 100 g. of finely ground urea were then quickly added; a vigorous reaction took place with considerable foaming and the evolution of large quantities of carbon monoxide and carbon dioxide. The temperature of the reaction mixture immediately rose to 55–60° and then with the help of a burner was brought to 75° and held there for thirty minutes. The straw colored reaction mixture was cooled and poured on 1200 g. of ice. On inoculation, uracil-4-acetic acid started to separate out at once and was completely separated on standing in the ice box for two days, yield of crude dry product 42–43 g. It was decolorized with bone black and recrystallized from water. When a hot water solution was rapidly cooled it separated in the anhydrous condition (fine needles); on very slow cooling, as the monohydrate (stout prisms); it did not melt at 300°.

Anal. Calcd. for $C_6H_6N_2O_4.H_2O$: H_2O, 9.58. Found: H_2O, 9.61. Calcd. for $C_6H_6N_2O_4$: C, 42.34; H, 3.56; N, 16.47. Found: C, 42.46, 42.40; H, 3.63, 3.80; N, 16.44.

The conditions (acidic) of the above reaction preclude the preparation of the analogous thiopyrimidines by the substitution of urea by thiourea. The preparation of 4-methyluracil and thymine from ethyl acetoacetate and ethyl sodiumformylpropionate, respectively, was unsuccessful; the conditions of the experiment were widely varied with respect to the strength of the sulfuric acid and the temperature at which the reaction was carried out. It was also impossible to synthesize quinolones by heating aniline with either malic or citric acid in fuming sulfuric acid.

Uracil-4-methylacetate.—Large blocky plates, m. p. 220°.

Anal. Calcd. for $C_7H_8N_2O_4$: N, 15.22. Found: N, 15.41, 15.23.

Uracil-4-ethylacetate.—It separated from a 50% alcohol–water solution as colorless plates containing one molecule of water of crystallization and melting at 191–192° (Wheeler and Liddle reported 187–188°).

Anal. Calcd. for $C_8H_{12}N_2O_5$: H_2O, 8.33. Found: H_2O, 8.55. Calcd. for $C_8H_{10}N_2O_4$: N, 14.14. Found: N, 14.24, 14.27.

The Action of Barium Hydroxide on Uracil-4-acetic Acid.—When a solution of uracil-4-acetic acid was mixed with a solution of barium hydroxide, there was no immediate precipitate. However, if this was warmed or allowed to stand for some time, an insoluble barium salt precipitated. This behavior would seem to indicate that the pyrimidine has been altered The barium salt was best obtained by the following procedure. Two grams of uracil-4-acetic acid was dissolved in 25 cc. of hot water and treated with a hot solution of 15 g. of barium hydroxide hydrate in 75 cc. of water. A clear solution resulted which, on standing overnight, precipitated star-like clusters of prisms, yield 2.9 g. It was insoluble in boiling water. The analysis agreed best with that of the barium salt of β-carbamidoglutaconic acid.

Anal. Calcd. for $C_6H_6O_5N_2Ba$: Ba, 42.47. Found: Ba, 42.25.

It dissolved readily in hot dilute hydrochloric acid and on cooling deposited uracil-4-acetic acid.

Orotic Acid.—A solution of 7.4 g. of uracil-4-acetic acid in 475 cc. of water was treated with 27.5 g. of potassium hydroxide and 78 g. of potassium ferricyanide. The reaction mixture was a dark reddish-brown, characteristic of this type of oxidation. It was allowed to stand at room temperature for twenty-two days; there was a slight decrease in the color of the solution at the end of this time. On acidification with acetic acid, considerable carbon dioxide was evolved and the brown potassium salt separated. This was allowed to stand for a few hours and filtered. The precipitate was recrystallized from boiling water and separated as star-like clusters of prisms; yield of potassium orotate 2.2 g. It was dissolved in water acidified with hydrochloric acid, cooled and filtered. The product after decolorization with bone black and recrystallization from water was compared optically with an authentic specimen. They were found to be identical. The crystals were biaxial negative, had a medium angle, and were strongly birefringent. The angle of extinction was either zero or very small. The low index was 1.66 and the high index was somewhat over 1.74.

Anal. Calcd. for $C_5H_4O_4N_2 \cdot H_2O$: H_2O, 10.35. Found: H_2O, 10.38. Calcd. for $C_5H_4O_4N_2$: C, 38.45; H, 2.58; N, 17.95. Found: C, 38.54, 38.60; H, 2.53, 2.56; N, 17.95, 17.99.

4,5-Dihydrouracil-4-ethylacetate.—A solution of 2.2 g. of ethyluracil-4-acetate in 100 cc. of warm alcohol was treated with 0.2 g. of platinum oxide and subjected to 42 pounds' pressure of hydrogen for twenty-four hours. The reaction at the end of this time was complete and the reduction product had crystallized out. It was brought into solution by heating and the platinum black removed by filtration. The filtrate was concentrated to 50 cc. and cooled. The 4,5-dihydrouracil-4-ethylacetate that separated was recrystallized from 25 cc. of ethyl alcohol, from which it separated as a mass of colorless prisms melting at 155–156°, yield 1.5 g.

Anal. Calcd. for $C_8H_{12}N_2O_4$: C, 47.98; H, 6.04; N, 14.00. Found: C, 47.92, 48.14; H, 6.16, 6.31; N, 14.08, 14.12.

3-Methyl-4,5-dihydrouracil.—This was prepared by reducing 6 g. of 3-methyluracil in the same manner as described above. The filtrate from the reduction mixture was

concentrated to 25 cc. and cooled; long thick needles separated. It was recrystallized from 25 cc. of hot alcohol, in which it was very soluble; m. p. 175–176°; the yield was very good.

Anal. Calcd. for $C_5H_8O_2N_2$: C, 46.84; H, 6.30; N, 21.87. Found: C, 47.15, 46.93; H, 6.27, 6.21; N, 21.89.

Summary

1. Uracil-4-acetic acid was prepared by treating urea and citric acid with fuming sulfuric acid. This pyrimidine ring was easily ruptured by barium hydroxide solution and yielded the barium salt of β-carbamidoglutaconic acid.

2. Orotic acid was synthesized by oxidizing uracil-4-acetic acid in alkaline solution with potassium ferricyanide.

3. The possibility that orotic acid may be an intermediate in the synthesis of purines from histidine has been discussed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

THE ACTION OF ACETIC ACID UPON CERTAIN CARBOHYDRATES[1]

BY H. T. CLARKE AND H. B. GILLESPIE

RECEIVED JANUARY 23, 1932 PUBLISHED MAY 7, 1932

It has been shown[2] that native cellulose is esterifiable by the action of boiling acetic acid to a limited extent represented in the formula $C_{24}H_{39}O_{20}(COCH_3)$, whereas hydrated cellulose under the same conditions can yield an ester of the limiting composition $C_{24}H_{36}O_{20}(COCH_3)_4$. A study of the behavior of other carbohydrates toward acetic acid was therefore undertaken in the hope of finding a clue to the nature of the factors which tend to restrict the esterifiability of cellulosic hydroxyl groups.

Reducing carbohydrates, such as glucose and fructose, caramelize under the influence of boiling acetic acid alone or in the presence of sodium acetate. This applies also to the two non-reducing carbohydrates of the furanose type which have been examined, namely, sucrose and inulin—a finding which need occasion no surprise, in view of the well-established ease with which the five-membered ring of sugars may be opened by acid reagents. The cyclic structure of non-reducing glycosides of the pyranose type, on the other hand, withstands the action of boiling acetic acid, and such compounds ultimately yield fully esterified products. Thus α-methylglucoside, β-methylglucoside and α-methylmannoside are converted into the corresponding tetraacetates, while potato starch yields a "triacetate." Similarly, mannitol is converted into its hexaacetate.

[1] Work supported by a research grant from The Chemical Foundation.

[2] C. J. Malm and H. T. Clarke, THIS JOURNAL, **51**, 274 (1929).

These experiments thus throw little light upon the problems raised by the case of cellulose, beyond adding indirect confirmation of the view advanced by Hess and Trogus[3] that reactions with undissolved cellulose take place upon micellar surfaces.

The results obtained with potato starch nevertheless offer a certain intrinsic interest. This starch, which appears[4,5,6] to contain 96 to 98% of β-amylose, is at first esterified on treatment with boiling acetic acid in much the same way (though far more rapidly) as is hydrated cellulose, yielding as a primary product a "monoacetate" $C_6H_9O_5(COCH_3)$. At this stage the starch becomes soluble in acetic acid, and esterification continues until the composition approximates that of the "triacetate" $C_6H_7O_5(COCH_3)_3$.

The general properties of the products at various stages are shown in Table I. The faculty of yielding a blue color with iodine disappears when about 6% of acetyl has been introduced, but returns on removal of the acetyl groups by alkaline hydrolysis, the regenerated starch closely resembling ordinary "soluble starch." Progressive esterification is

TABLE I

Hours	% Acetyl	Acetic acid	Pyridine	Acetone	Ethyl acetate	Benzene	$CHCl_3$	85% $CHCl_3$—15% EtOH	$C_2H_2Cl_4$	Ac_2O	Dioxane	75% EtOH-H_2O	50% EtOH-H_2O	25% EtOH-H_2O	H_2O	Color with iodine	$[\alpha]_{546}$ in pyridine	Reducing power (as % glucose)
1	4.6	−	−	−	−	−	−	−	−	−	−	−	−	−	±	Blue		−
2	6.0	−	±	−	−	−	−	−	−	−	−	−	−	−	+	Red		−
4	10.6	−	+	−	−	−	−	−	−	−	−	−	±	+	+	Brown		0
	20.5	+	+	−	−	−	−	−	−	−	−	±	+	+	+	Brown		−
8	19.7	−	+	−	−	−	−	−	−	−	−	±	+	+	+	Brown		−
	21.4	+	+	−	−	−	−	−	−	−	−	±	+	+	+	Brown		0
12	23.3	−	+	−	−	−	−	−	−	−	−	+	+	+	+	Brown	+163° (21)	−
	25.7	+	+	−	−	−	−	±	−	−	±	+	+	±	+	Brown	+172° (21)	−
18	27.7	+	+	+	−	−	−	+	−	−	+	+	+	±	±	Brown	+175° (22)	0
24	30.1	+	+	+	−	−	−	+	−	−	+	+	+	±	±	Brown	+187° (19)	−
36	31.3	+	+	+	−	−	−	+	−	−	+	+	+	−	−	Brown	+192° (19)	−
48	34.4	+	+	+	+	−	+	+	±	+	+	+	+	−	−	Brown	+187° (19)	0
72	35.4	+	+	+	+	−	+	+	+	+	+	+	+	−	−	Brown	+187° (21)	0.27
96	37.9	+	+	+	+	−	+	+	+	+	+	+	−	−	−	Brown		−
144	41.0	+	+	+	+	−	+	+	+	+	+	+	−	−	−	Brown		0.61
192	41.7	+	+	+	+	−	+	+	+	+	+	±	−	−	−	Brown		−
224	43.4	+	+	+	+	±	+	+	+	+	+	±	−	−	−	Brown		−
296	44.0	+	+	+	+	±	+	+	+	+	+	−	−	−	−	Brown		0.66
620	44.1	+	+	+	+	±	+	+	+	+	+	−	−	−	−	Brown		−

[3] Hess and Trogus, *Z. physik. Chem.*, **15**, 157 (1931).

[4] Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

[5] Haworth, Hirst and Webb, *J. Chem. Soc.*, 2681 (1928).

[6] Baldwin, THIS JOURNAL, **52**, 2907 (1930).

accompanied by increasing solubility in non-polar solvents, though in no case was solubility in 95% ethyl alcohol or ethyl ether observed. The lower esters are soluble in water; those of intermediate composition are soluble in aqueous ethyl alcohol of various ranges of concentration.

The products obtained by boiling potato starch with acetic acid alone for seventy-two hours and more yield, on alkaline hydrolysis, solutions possessing reducing power, the extent of this increasing with the duration of the treatment. This effect appears to be mainly due to the degrading action of the phosphoric acid which exists in combination with the 3% of α-amylose present in the starch, and may be largely suppressed by the addition of sodium acetate. In Table II are summarized the results of an experiment in which 110 g. of potato starch was boiled with 2200 cc. of acetic acid containing 1 g. of sodium acetate. The reducing power, estimated by the method of Folin and Wu,[7] is expressed as percentage of glucose in the starch acetate; detectable reduction occurred only with products obtained on boiling for 192 hours or more. Addition of the sodium acetate markedly retards the rate of esterification.

TABLE II

Time heated, hours	Acetyl, %	Solubility in acetic acid	Reducing power	Time heated, hours	Acetyl, %	Solubility in acetic acid	Reducing power
4	0.6	−	0	48	29.8	+	0
8	7.5	−	0	96	34.8	+	0
12	15.5	−	0	144	37.3	+	0
12	18.6	+	0	192	41.2	+	0.16
18	23.6	+	0	288	41.6	+	.32
24	27.1	+	0	384	43.3	+	.23

Apart from its reducing properties, the final product of the action of boiling acetic acid upon potato starch resembles the starch triacetates obtained by the methods of other workers, particularly that of Tsuzuki.[8] A triacetate of the same general properties, but lacking reducing power, may also be prepared by boiling the starch with acetic acid until it has dissolved and then completing the acetylation with acetic anhydride; we believe that this two-step process provides the most convenient method for preparing a starch triacetate. The products obtained by the methods of Haworth, Hirst and Webb[5] and of Hess and Smith[9] appear to be somewhat less degraded, inasmuch as they dissolve less readily and less completely in organic liquids.[10]

Table III shows the acetyl contents, reducing power and rotation in three solvents of triacetates obtained by various methods from the same

[7] Folin and Wu, *J. Biol. Chem.*, **41**, 367 (1920). The authors are indebted to Miss Rhoda Howard for kindly making these determinations.

[8] Tsuzuki, *Bull. Chem. Soc. Japan*, **3**, 276 (1928).

[9] Hess and Smith, *Ber.*, **62**, 1619 (1929).

[10] *Cf.* Brigl and Schinle, *ibid.*, **62**, 99 (1929).

sample of potato starch. With the exception of the product prepared according to the directions of Hess and Smith, which gelatinized rather than dissolved in pyridine and chloroform, the solubilities were roughly the same in every case.

TABLE III

Method of preparation	% Acetyl,	Reducing power	$[\alpha]_{546}$ in Pyridine	Chloroform	Acetic acid
Haworth, Hirst and Webb	41.2	0	+129° (28°)	Turbid	+142° (17°)
Hess and Smith	44.5	0	Turbid	Turbid	Turbid
Tsuzuki	46.1	0	179° (25°)	193° (25°)	183° (17°)
Boiled 28 hours AcOH then $Ac_2O + C_5H_5N$	44.5	0	174° (20°)	197° (21°)	184° (20°)
Boiled 384 hours AcOH + AcONa					
Fraction 1	43.0	0.52	194° (19°)	198° (21°)	196° (19°)
Fraction 2	43.5	0.17	189° (22°)	196° (22°)	189° (22°)

Experimental

The method of acetyl determination was in all cases essentially the same as that adopted for the cellulose derivatives.

α-Methylglucoside Tetraacetate.—A mixture of 50 g. of α-methylglucoside and 500 cc. of glacial acetic acid was boiled under reflux in an all-glass apparatus. After twenty-four hours the acid was distilled through a column until the temperature of the vapor reached 115°. The distillate amounted to 175 cc.; this volume of glacial acetic acid was replaced in the reaction mixture and the boiling under reflux continued for forty-eight hours longer. On distilling off the moist acid up to 115°, 125 cc. of distillate was obtained and a similar volume of fresh acid replaced. This process was continued, moist acid being removed at increasing intervals until boiling had been continued for a total time of 240 hours. The acetic acid was then removed by distillation under reduced pressure, the dark brown viscous residue was dissolved in ethylene chloride and this solution shaken with dilute potassium carbonate, filtered, separated and distilled under reduced pressure from the steam-bath. The residue, weighing 81 g., was distilled under 4 mm. pressure, when 64 g. of a pale yellow, very viscous oil passed over at 158–160°. This contained 47.7% acetyl (calculated for $C_7H_{10}O_6(COCH_3)_4$, 47.5%). This distillate remained liquid almost indefinitely at room temperature if not inoculated. On addition of a crystal of α-methylglucoside tetraacetate it crystallized very slowly, becoming completely solid only after a lapse of several months. It was, however, rapidly converted into the crystalline form by rubbing under cold water with a crystal of the tetraacetate. After one recrystallization from alcohol it melted at 100.5–101.5° and showed no depression of melting point when mixed with authentic α-methylglucoside tetraacetate. On hydrolysis of a sample of the sirupy product by means of alcoholic barium hydroxide, α-methylglucoside, m. p. 166°, was regenerated.

β-Methylglucoside Tetraacetate.—By heating 10 g. of β-methylglucoside and 200 cc. of acetic acid, as above, for 240 hours (acetyl content after 144 hours, 41.0%). Distilled product (b. p. 185–187° (5 mm.)) analyzed 46.9% acetyl (calcd. 47.5%) and crystallized on inoculation, m. p. 101–102.5°, from toluene; did not depress melting point of a sample prepared with acetic anhydride.

α-Methylmannoside Tetraacetate.—From 50 g. of α-methylmannoside and 500 cc. of acetic acid for 144 hours; b. p. 204–207° (5 mm.), contained 47.6% acetyl; m. p. 65–66° from alcohol; mixed m. p. 65–66°.

Mannitol Hexaacetate.—From mannitol and 10 parts of acetic acid for 240 hours;

crystallized on concentrating the reaction mixture; m. p. 119°;[11] acetyl 59.2% (calcd. 59.5%).

Acetylation of Potato Starch.—Commercial potato starch, containing about 12% of moisture, was suspended in twenty times its weight of glacial acetic acid and heated to boiling. Continual mechanical stirring was necessary to avoid bumping. The water was removed at the outset and then at frequent intervals, the distillates being replaced by equal volumes of glacial acetic acid. Samples were withdrawn periodically; during the first eighteen hours the undissolved portions were separated by centrifuging and well washed with acetic acid; the solution was freed of the bulk of the acetic acid by distillation under reduced pressure and the residue precipitated by means of 95% ethyl alcohol. Subsequently, samples of the homogeneous solution were merely concentrated under reduced pressure and precipitated with alcohol. The products were repeatedly washed with alcohol until free of acetic acid and then dried *in vacuo* over phosphorus pentoxide.

Rotations were determined on samples obtained after twelve to seventy-two hours' boiling; those secured after longer periods were too dark to read. The material produced by boiling for 384 hours in the presence of sodium acetate (Table II) was subjected to fractional precipitation, and so obtained free of color. The dark solution in acetic acid was slowly diluted with water until about half of the dissolved ester had precipitated. The supernatant liquor, containing 53% of acetic acid, was practically colorless; on dilution with much water it yielded Fraction 1. The first precipitate was then dissolved in ethyl acetate and ether added to the solution until the supernatant portion was colorless. This process was repeated six times with the dark coagulum. The clear solution was concentrated to a small volume and treated with excess of ether, when Fraction 2 precipitated. The dark, gummy residue was discarded. The properties of Fractions 1 and 2 are shown in Table III.

Preparation of Starch Triacetate.—A suspension of 50 g. of potato starch (containing 12% moisture) in 1000 cc. of acetic acid containing 1 g. of sodium acetate was boiled under reflux, with stirring, for twenty-eight hours, aqueous acetic acid being periodically removed and replaced with anhydrous acid. The volume was then reduced to 500 cc. by distillation under diminished pressure. The residual clear solution was mixed with 150 cc. of 95% acetic anhydride and 75 cc. of pyridine, and boiled for six hours. The volume was then reduced, by distillation under diminished pressure, to about 200 cc., and the sirupy residue was poured into a liter of ice water. The granular precipitate was well washed with water and then with alcohol, and dried *in vacuo* over phosphorus pentoxide. The starch triacetate (44.5% acetyl) weighed 76.6 g. (98% of the theoretical amount); it was readily soluble in acetic acid, chloroform, dioxane, ethyl acetate and pyridine, almost completely in acetone, slightly in benzene, insoluble in ethyl alcohol, ethyl ether and water. Other properties are recorded in Table III.

Summary

On treatment with boiling acetic acid:

1. Reducing carbohydrates and the non-reducing furanoses, sucrose and inulin, caramelize.

2. Mannitol and non-reducing glycosides of the pyranose type become fully esterified.

3. Potato starch yields a continuous series of amorphous acetates, the acetyl content of which increases with time of treatment and reaches

[11] Bouchardat, *Ann. chim.*, [5] **6**, 107 (1875), reports 119°.

a limit with the introduction of three acetyl groups for each glucose residue.

NEW YORK CITY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 79]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. XII. THE PREPARATION AND PROPERTIES OF MIXED ALIPHATIC ETHERS WITH SPECIAL REFERENCE TO THOSE CONTAINING THE TERT.-BUTYL RADICAL

BY JAMES F. NORRIS AND GEORGE WAYNE RIGBY[1]

RECEIVED JANUARY 26, 1932 PUBLISHED MAY 7, 1932

The influence of structure on the lability of bonds in organic molecules is shown in a marked degree by compounds which contain a tertiary radical. For example, the *tert.*-butyl alcohol reacts with concentrated hydrochloric acid over 200,000 times as rapidly as does *n*-butyl alcohol. It seemed of interest, therefore, to determine whether or not the facts accumulated in connection with the study of the lability of the carbon–oxygen and of the hydrogen–oxygen bonds in alcohols[2] by means of rates of reaction could be utilized in devising improved methods for the preparation of ethers and esters. A study of these classes of compounds from the standpoint of their relative reactivities with reagents would lead to a fuller understanding of the influence of structure on the lability of atomic linkings.

Certain *tert.*-butyl alkyl ethers have been prepared by the commonly used methods, but the results, as measured by yields and purity, have been far from satisfactory. One of the methods used is based on the view that the mechanism of ether formation from alcohols involves the intermediate formation of an alkyl sulfuric acid and consequently concentrated sulfuric acid was used to bring about the reaction between *tert.*-butyl alcohol and ethyl alcohol. Since the acid rapidly converts the tertiary alcohol into polymers of isobutylene, the yields obtained were very small.

When the Williamson synthesis is used difficulties are encountered as the result of the unique behavior of compounds containing a tertiary radical. Sodium *tert.*-butylate is formed very slowly and reacts very slowly with alkyl halides. The chief reaction between tertiary alkyl halides and the sodium derivatives of normal alcohols is the removal of hydrogen halide from the alkyl halide. When these methods are used the yields are also very small.

[1] From the thesis of George Wayne Rigby submitted in partial fulfilment of the requirement for the degree of Doctor of Philosophy, 1930.

[2] (a) Norris, *Rec. trav. chim.*, **48**, 885 (1929); (b) Norris, *Z. physik. Chem.*, **130**, 662 (1927); (c) Norris and Ashdown, THIS JOURNAL, **47**, 837 (1925); (d) Norris and Cortese, *ibid.*, **49**, 2640 (1927).

It seemed probable that advantage could be taken of the great reactivity of the hydroxyl group in *tert.*-butyl alcohol and of the alcoholic hydrogen in primary alcohols in the preparation of mixed ethers through the catalytic influence of dilute acids in the way used to prepare esters.

A series of experiments showed that mixed ethers containing the *tert.*-butyl and primary alkyl radicals could be readily prepared in this way. The best yield of *tert.*-butyl ethyl ether, 95% of the theoretical, was obtained when one mole of the tertiary alcohol was added slowly to a boiling mixture of two moles of ethyl alcohol and a 15% aqueous solution of sulfuric acid, the volume of which was about 2.5 times that of the ethyl alcohol. The vapors were passed through a column at such a rate that the minimum boiling mixture of the ether and water was allowed to pass over. Other mixed *tert.*-butyl ethers containing primary radicals were prepared in a similar way.

The fact that the hydrogen of the hydroxyl group in secondary alcohols is much less reactive than the corresponding atoms in primary alcohols necessitated a change in conditions where an attempt was made to prepare *tert.*-butyl isopropyl ether. When 15% sulfuric acid was used the reaction was very slow with the resultant formation of large quantities of isobutylene. In order to increase the rate, a greater molecular ratio of the secondary alcohol was used and to decrease the decomposition of the tertiary alcohol an aqueous solution of sodium hydrogen sulfate was employed as the catalyst. The yield of the mixed ethers was 82% of the theoretical.

The formation of mixed ethers containing secondary and primary alkyl radicals was next investigated. The reactivity of the hydroxyl group in secondary alcohols is very much less than that of the same group in tertiary alcohols. The results of the study of the preparation of ethers of this class were found to be in accord with this fact. Much higher concentrations of sulfuric acid were required to bring about the reaction. The product in all cases was a mixture of the three possible ethers. The differences between the reactivities of the hydroxyl groups in primary and secondary alcohols is not sufficiently great to lead to the formation of only the mixed ether as was the case when *tert.*-butyl alcohol was used. By varying the amount and the concentration of sulfuric acid the ratio of mixed ether to simple ethers could be changed. In one experiment with *sec.*-butyl alcohol and ethyl alcohol when 50% sulfuric acid was used the total yield of the three ethers amounted to 49.5% of the theoretical of which 8% was diethyl ether and 72.5% *sec.*-butyl ethyl ether. The tendency for a larger proportion of the mixed ether to form is in accord with the differences in reactivity of the hydroxyl group and the hydrogen atoms in primary and secondary alcohols.

A number of ethers were prepared by the methods outlined above and by the application of the Williamson synthesis, which gave satisfactory

results when primary and secondary alcohols were used. Especial care was taken to obtain the ethers in a very pure condition since the physical constants recorded in the literature are not concordant. The boiling points, densities and indices of refraction were determined and are recorded in the experimental part of this paper.

One of the chief objects of this research was the study of ethers containing two different alkyl radicals to determine if their reactions are in accord with the relative reactivities of the carbon–oxygen bonds present as determined by a study of the rates at which these bonds react when present in the corresponding alcohols. It was expected that the ethers containing the *tert.*-butyl radical would show unusual reactivity, and the results proved to be in accord with the expectation. The reactions studied were those with hydrochloric acid, sulfuric acid, acetic acid, acetyl chloride, benzoyl chloride and acetic anhydride.

The aliphatic ethers are more or less soluble in solutions of hydrochloric acid. It has been shown that certain ethers form molecular compounds with hydrogen chloride at low temperatures.[3] It is highly probable that these addition products are oxonium compounds. It is possible that such compounds are formed when ethers dissolve in aqueous solutions of hydrochloric acid. It is to be expected that the tendency of the oxygen atom in ethers to form oxonium compounds would vary with the radicals which they contain. A quantitative study of the solubilities of the isomeric butyl ethyl esters was accordingly made. The solubility of an ether is determined by the concentration of the acid and the temperature. The results are shown in Figure 1. The relative solubilities of the butyl ethyl ethers in the same concentration of acid and at a definite temperature vary markedly with the structure of the butyl radicals. The solubilities show a striking relationship with the labilities of the bond linking the butyl radicals to the oxygen atom, the more labile the bond the greater the solubility. If oxonium compounds are present in the solution, it follows that the tendency for oxygen to exhibit oxonium valencies is determined by the lability of the bond linking the oxygen atom to carbon—the more reactive this bond, as measured by the rate at which it is broken by hydrochloric or hydrobromic acid, the greater the tendency to form oxonium compounds with hydrochloric acid.

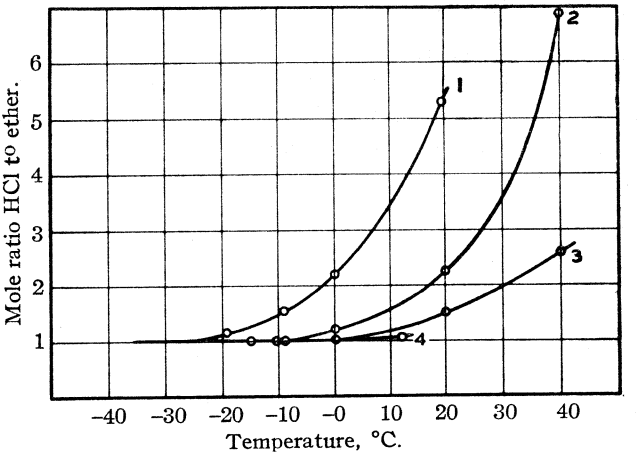
It is a striking fact that with decreasing temperature the molecular ratio of the ether to hydrogen chloride in the solution approaches one to one.

The isomeric butyl ethyl ethers react extremely slowly at room temperature with concentrated hydrochloric acid, with the exception of the *tert.*-butyl compound. When *tert.*-butyl ethyl ether and concentrated hydrochloric acid in the molecular ratio of one of the former to five of the latter are mixed the ether dissolves, but is rapidly converted into *tert.*-butyl

[3] Maass and McIntosh, THIS JOURNAL, **34**, 1274–1290 (1912).

chloride, which separates. When such a mixture was allowed to stand overnight 99% of the theoretical quantity of the chloride was obtained.

In order to get a definite idea of the effect of the structure of the butyl radical on the lability of the carbon–oxygen linkage in these ethers, the rates of the reactions with hydrochloric acid at 25° were measured. The ethers were dissolved in the acid in a vessel so constructed that the volume of the chloride formed could be measured. The tubes were sealed, placed in a thermostat and the volume of chloride noted from time to time. Density determinations of the products showed that they were the pure butyl chloride corresponding to the ether used.



(1) *Iso*-butyl ethyl ether, (2) *n*-butyl ethyl ether, (3) *sec.*-butyl ethyl ether, (4) *tert.*-butyl ethyl ether.

Fig. 1.—Solubilities of isomeric butyl ethyl ethers in 35.21% hydrochloric acid.

There was an induction time before the chlorides separated. In order to have the results comparable zero time was taken when a measurable amount of chloride had separated—1 to 3% of the theoretical amount. When velocity constants were calculated on the assumption that the reaction was one either of the first or second order, the values of the constants obtained dropped off rapidly after 50% of the calculated amount of chloride had separated. In order to avoid postulation in regard to the order of the reaction as the cause of the change in the value of the constant, the results are represented in Table I as time required for the several reactions to proceed to the extent of 25%. These values serve to compare the relative reactivities of the bonds involved.

Experiments 1, 2 and 3 show the effect of change in structure of the butyl radical on the rate at which the carbon–oxygen bond is broken by concentrated hydrochloric acid with the consequent formation of the

TABLE I

FORMATION OF BUTYL CHLORIDES FROM THE ISOMERIC BUTYL ETHYL ETHERS

No.	Compound	Temp., °C.	Mol. ratio compd. to HCl	Concn. of HCl, %	Time in hours to 25% conversion
1	*n*-Butyl ethyl ether	25.0	1:18.8	35.21	768
2	*Sec.*-butyl ethyl ether	25.0	1:18.8	35.21	105
3	*Iso*-butyl ethyl ether	25.0	1:18.8	35.21	1250
4	*Tert.*-butyl alcohol	0.0	1:10	26.75	1.6
5	*Tert.*-butyl methyl ether	.0	1:10	26.75	3.5
6	*Tert.*-butyl ethyl ether	.0	1:10	26.75	0.83

butyl chlorides. The order of reactivity is the same as that previously obtained in the study of the rates at which the corresponding butyl alcohols react with aqueous solutions of hydrobromic acid, with the formation of the butyl bromides.

The tertiary butyl ethers react so rapidly with concentrated hydrochloric acid at 25° that it was necessary to study them under different conditions. Experiments 4, 5 and 6 show the effect of the change from H to CH_3 and to C_2H_5 on the lability of the bond linking the carbon atom of the butyl radical to oxygen. The results bring out an important point. When the alcoholic hydrogen atom in methyl alcohol and that in ethyl alcohol are replaced by a *p*-nitrobenzoyl radical, the former reacts about twice as rapidly as the latter.[2c] The results in the table show that when similar ethers of these alcohols are converted into the respective alcohols the ethyl ether reacts almost five times as rapidly as the methyl ether. When RO—H is converted into RO—R′ the reaction is more rapid when R is CH_3 than when it is C_2H_5. When RO—R′ is converted into RO—H the reverse is true. These results bring out the important fact, often overlooked, that the relative lability of a bond, as measured by rates of reactions, is not a fixed property of the radical but is determined both by the nature of the radical itself and the nature of the group with which it is brought into combination in the reactions studied. It has been shown, for example, that *tert.*-butyl chloride reacts much more rapidly with water than does *n*-butyl chloride, but that the tertiary chloride reacts more slowly with potassium iodide than does the normal chloride.[4] The relative lability of the carbon–chlorine bonds in the two chlorides is different when measured by different reagents. In one case chlorine is replaced by hydroxyl and in the other by iodine. It should be noted in this connection that *tert.*-butyl alcohol reacts rapidly with hydrochloric acid, whereas it reacts much more slowly with hydriodic acid. These facts and those of a similar nature must be considered in comparing the relative activating effects of radicals on atomic linkings.

The action of sulfuric acid with the ethers was studied. One mole

[4] Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

of normal or isobutyl ethyl ether dissolves in one mole of concentrated sulfuric acid. When ice is added to the mixture the ethers are recovered unchanged. All the *tert.*-butyl ethers are quickly decomposed by concentrated sulfuric acid. If the temperature of the mixture is allowed to rise the higher polymers of isobutylene are obtained. If the reactants are cooled to 0° and mixed so that the temperature does not rise, the polymer formed is almost entirely tri-isobutylene. When heated with dilute sulfuric acid (10%) the tertiary ethers are slowly hydrolyzed; at the same time some isobutylene is formed.

All the butyl ethyl ethers react at room temperature with acetyl chloride in the presence of zinc chloride. Two reactions occur: the one yielding *n*-butyl chloride and ethyl acetate takes place to the extent of 34%, and the one yielding ethyl chloride and *n*-butyl acetate, 58%. Both the ethyl–oxygen and the *n*-butyl–oxygen bonds are broken. At 60° the chief products are ethyl chloride and butyl acetate. The effect of increase in temperature on the relative labilities of the two bonds is marked in the case of the two normal radicals.

At room temperature isobutyl ethyl ether gives chiefly isobutyl acetate and ethyl chloride. At 80° the reaction produced a number of products among which were *tert.*-butyl chloride and isobutylene. The bond broken in the ethers containing secondary and tertiary radicals is the one between these radicals and oxygen. *Sec.*-butyl ethyl ether at room temperature in the presence of zinc chloride gave only *sec.*-butyl chloride and ethyl acetate. *Tert.*-butyl ethyl ether under these conditions reacted rapidly and gave a theoretical yield of *tert.*-butyl chloride and ethyl acetate.

Acetic anhydride did not react with the ethers at room temperature or at 100° in the absence of a catalyst. Reaction did take place slowly at room temperature in the presence of zinc chloride. In all cases the pure acetates containing the two radicals were formed.

New methods of preparing *tert.*-butyl acetate which yielded the compound in a state of high purity are described in the experimental part of this paper. The ester was converted rapidly by concentrated hydrochloric acid into *tert.*-butyl chloride and acetic acid. The preparation and properties of *tert.*-butyl benzoate, prepared for the first time, also are given.

The work shows clearly the practical value from the standpoint of the synthesis of organic compounds of the results obtained from the study of the reactivity of bonds as measured by rates of reactions. They also give additional information in regard to the mechanism of ether formation under the influence of sulfuric acid. The older view of Williamson that an alkyl sulfuric acid is formed as an intermediate product does not appear to apply in the case, at least, of the ethers containing the *tert.*-butyl radical. Experiments showed that there was no evidence of the formation of an

alkyl sulfuric acid when ethyl alcohol alone, or mixed with *tert.*-butyl alcohol, was heated at 70° with 15% sulfuric acid. The solutions when cooled and carefully titrated showed the presence of the amount of sulfuric acid used. The fact that primary, secondary, and tertiary alcohols required different strengths of acid to bring about the formation of ethers is in accord with the relative stabilities toward water of the addition products of the alcohols and sulfuric acid.

Even in the case of a primary alcohol it is doubtful whether or not the mechanism involves the intermediate formation of an alkyl sulfuric acid. It has been shown by Barbet[5] that diethyl ether is best prepared, with a yield of 95% or better, when alcohol is passed through concentrated sulfuric acid heated to 140°. When alcohol vapor was passed into ethyl sulfuric acid at the same temperature the yield was 70% and much sulfur dioxide was evolved.

Experimental Details

Materials Used.—The most convenient way to purify the four butyl alcohols is to fractionate their constant boiling mixtures with water. The products obtained in this way, which boiled within 0.5°, were dried, first with potassium carbonate and then with lime, and were fractionated. The alcohols obtained boiled within 0.1°.

In some of the larger scale preparations involving the use of *tert.*-butyl alcohol, a commercial sample of the alcohol was used, which was found to contain 10% of water but was otherwise quite pure.

The acetic anhydride when distilled in an all-glass apparatus boiled at 137°. The acetyl chloride was obtained from a so-called "practical" sample. Seven distillations with precautions against superheating were necessary to obtain a product that boiled constantly at 50.9° (corr.) at 760 mm. and had the density d_4^{25} 1.0922. The chloride reacted very slowly when added to a large volume of cold water. A sample remained in contact with bright sodium chips for nine months at room temperature without apparent action. Care was used in the preparation because the constants given in the literature are not concordant and because it was found that the presence of impurities in the chloride affected its behavior with the ethers studied. The boiling point obtained agrees with that given by Thorpe.[6]

The benzoyl chloride used boiled at 198° at 760 mm. and at 77° at 2 mm. pressure.

The alkyl halides were prepared from the alcohols and aqueous solutions of the acids and gave constants in agreement with the literature.

Determination of Boiling Points.—Distillations were carried out through columns of the Vigreux type fitted with condensing heads and covered with insulating material. In the final purifications and the determinations of boiling points vacuum jacketed spiral columns of the Davis[7] type were used.

In the distillations heat was supplied from an electric heater connected in series with a slide-wire rheostat. Attention was paid to the heat furnished and the amount of reflux. Under the conditions used the flat portion of a distillation curve of the pure compound included almost the entire sample, with a variation in temperature of less than 0.05°.

[5] Barbet, British Patent 100,406 (1915) and 101,724 (1916).

[6] T. E. Thorpe, *J. Chem. Soc.*, **37**, 188 (1880).

[7] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

The distillation curve of a sample of *tert.*-butyl ethyl ether serves to detect the presence of a trace of *tert.*-butyl alcohol, which can be separated only with great difficulty. The shape of the curve makes it possible to detect as little as 0.05% of the alcohol and a smaller quantity of water.

The physical constants of the *tert.*-butyl ethers reported in the literature show that the compounds have not been hitherto prepared in a state of purity. Samples prepared by the published methods gave the constants reported, but when distillation curves were made the presence of impurities was evident. The behavior of the ethers with certain reagents is affected by the presence of these impurities.

The careful study of the problem leads to the conclusion that accurate distillation curves made with an efficient column are a better criterion of purity than density determinations. Bennett and Philip,[8] who worked with *tert.*-butyl methyl ether, have expressed the opinion that density is a better criterion of purity than boiling point.

All accurate boiling points were determined with short range "normal glas" Anschütz thermometers, graduated to 0.2°. They were compared with thermometers calibrated by the Reichsanstalt and by the United States Bureau of Standards. Corrections were made for atmospheric pressure.

Determinations of Density.—These determinations were made with a glass-stoppered Sprengel tube having a capacity of about 13.5 cc. The temperature was 25 ± 0.005°. The weights were checked against a set calibrated by the United States Bureau of Standards. Densities are reported to the fourth decimal place and appear to be accurate to 2 in this place.

Preparation of *Tert.*-butyl Ethers.—*Tert.*-butyl methyl ether was made by the methods described in the literature. The preparation from sodium *tert.*-butylate and methyl iodide[9] gave a yield of 60% of a product which boiled at 53–55°, and was difficult to purify. The yield, by similar methods, of the ethyl ether was 50%, of the *n*-propyl ether 25% and the *n*-butyl ether 65%.

Tert.-butyl ethyl ether was also prepared by the action of a small amount of concentrated sulfuric acid on the two alcohols.[10] The yield of the crude ether was 48%.

Since these methods were not entirely satisfactory, the effect of other catalysts was studied. Potassium hydrogen sulfate gave good results. When a mixture of 10 cc. of commercial 90% *tert.*-butyl alcohol, 6 cc. of ethyl alcohol (95%) and 1.3 g. of powdered potassium hydrogen sulfate was distilled very slowly, the yield of crude ether (b. p. 64 to 70°) was 91% of the theoretical.

The best practical method of preparation was found to involve the use of dilute sulfuric acid as a catalyst. In this way the methyl, ethyl, *n*-propyl and *n*-butyl ethers derived from *tert.*-butyl alcohol were prepared. The details of the preparation of one ether by this process which is new, are given below.

Preparation of *Tert.*-butyl Ethyl Ether.—In a 3-liter flask are mixed 988 cc. of distilled water and 98 cc. of pure sulfuric acid (sp. gr. 1.84). When the solution has cooled, 0.5 g. of powdered silicic acid to ensure regular boiling and 450 cc. of 95% ethyl alcohol are added. The flask is attached to a 2-bulb Wurtz column by means of a stopper which carries a 100-cc. separatory funnel and a thermometer. A thermometer is inserted in the column, which is connected with a condenser and heat is applied. When the temperature in the flask reaches 70°, 100 cc. of *tert.*-butyl alcohol (90%) is added from the funnel. The product is distilled slowly, care being taken by the regulation of the supply of heat to keep the temperature of the issuing vapors at 64°, which is the boiling point of the minimum boiling mixture of the ether and water. From 0.5 to 0.75

[8] Bennett and Philip, *J. Chem. Soc.*, 1930 (1928).

[9] Henry, *Rec. trav. chim.*, **23**, 329 (1904).

[10] Mamontroff, *J. Russ. Phys.-Chem. Soc.*, **29**, 230 (1897).

cc. of distillate collects per minute. From time to time 25 cc. of the butyl alcohol is added until the total amount is 350 cc. The final distillate measures about 460 cc.

The product is washed in a separatory funnel repeatedly with 25 cc. of water. From ten to fifteen treatments are necessary to remove the last traces of *tert.*-butyl alcohol. When all the alcohol has been removed, the two layers separate instantly and completely, leaving the ether layer absolutely clear. The product is shaken with potassium carbonate and finally dried by refluxing over sodium for one hour. The pure ether boils at 73.1°. The yield is 95% of the theoretical calculated from the *tert.*-butyl alcohol used.

In the above directions the alcohols are in ratio of approximately one of butyl alcohol to two of ethyl alcohol. The excess of the latter serves to hasten the reaction and diminishes the formation of isobutylene. An efficient column is not advisable during the preparation as it holds back the ether and partial decomposition takes place in the flask. The distillation should not be stopped and the mixture left overnight because 15% sulfuric acid in the presence of ethyl alcohol slowly converts *tert.*-butyl alcohol, on standing, into isobutylene and its polymers.

If larger quantities of the crude ether are to be separated from *tert.*-butyl alcohol, it is preferable to redistil the product with a large amount of water and collect a second time the minimum boiling mixture of the ether.

A saturated aqueous solution of *tert.*-butyl ethyl ether contains at 25° 1.3% and at 0° 3.4% of the ether.

According to Henry[9] *tert.*-butyl methyl ether reacts slowly with sodium. This observation was no doubt due to the fact that the sample studied contained some of the butyl alcohol from which it was prepared. A sample of the highly purified ether was heated with sodium in a sealed tube at 90° for six weeks; only slight superficial action on the metal was observable.

The preparations of the following mixed ethers containing the *tert.*-butyl radical were made according to the directions just given, using the alcohols in the molecular ratio of one of the tertiary to two of the primary alcohol: methyl, *n*-propyl, and *n*-butyl. On account of the boiling points, the tertiary alcohol must be added very slowly in the preparation of the *n*-butyl ether. The yields of the purified ethers were CH_3, 95%; C_2H_5, 95%; *n*-C_3H_7, 68%; *n*-C_4H_9, 51.5%.

Preparation of Tert.-butyl Isopropyl Ether.—Isopropyl alcohol reacts with *tert.*-butyl alcohol more slowly than does *n*-propyl alcohol. When the ether is prepared under the conditions used in making the *n*-propyl compound, the yield is reduced as the result of the formation of isobutylene by the long continued action of the dilute sulfuric acid. It was found that an aqueous solution of sodium hydrogen sulfate gave excellent results. The ether was prepared as follows.

In a 500-cc. flask with three necks were placed 120 cc. of water, 22 g. of sodium hydrogen sulfate, 70 cc. of isopropyl alcohol and 0.5 g. of silicic acid. In one neck of the flask was placed a 2-bulb Wurtz column, in the second a dropping funnel and in the third a thermometer which extended into the liquid. Heat was applied and 50 cc. of *tert.*-butyl alcohol (90%) allowed to drop in slowly during ten hours. The distillate boiling at 70–71° was collected. The yield of the crude ether was 82% of the theoretical. The product was purified in the way described above. The ether boiled at 87.6° and had the density 0.7365_4^{25}.

Henry[11] reports that this ether boils at 75–76° and has the density 0.7734^{20}. We obtained a product that boiled constantly at 77.2° and had the density 0.7543_4^{25}. It reacted rapidly with sodium, however. After repeated treatment with the metal the ether had the boiling point and density recorded above. It was not affected by sodium.

[11] Henry, *Rec. trav. chim.*, **23**, 329 (1904).

n-**Butyl Ethyl Ether.**—This ether was prepared from sodium butylate and ethyl bromide. It was purified by shaking with a mixture of one volume of sulfuric acid and one volume of water and by fractional distillation. Its physical properties are given in Table II.

Preparation of Sec.-butyl Ethyl Ether.—This compound has not been described. It was prepared as follows: to 1 liter of anhydrous *sec.*-butyl alcohol (b. p. 99.5°) was added 8.5 g. of sodium. When the metal had dissolved, 25 cc. of pure ethyl bromide was added and the mixture allowed to stand for two days. Ten grams of sodium was added and later 25 cc. of ethyl bromide and the mixture allowed to stand for two days. The process was repeated until 175.5 cc. of ethyl bromide had been used. The product was distilled and the part boiling between 80 and 85° collected. This was mixed with 1 liter of water, distilled, and the portion boiling at 67–72° collected. This was redistilled with water and the portion boiling at 71–72° collected. The ether was separated, dried, refluxed with sodium and fractionated. The physical properties are given in Table II.

Preparation of Sec.-butyl Ethyl Ether with Sulfuric Acid as Catalyst.—The formation of an ether from a secondary and a primary alcohol requires a much higher concentration of sulfuric acid than is needed when one of the reactants is tertiary alcohol. A series of experiments was made with 25 cc. of *sec.*-butyl alcohol and 25 cc. of ethyl alcohol. When 100 cc. of 25% sulfuric acid was used, no ether was formed. With 400 cc. of 40% acid the yield was 5.5%. With 300 cc. of 50% acid the yield of the three ethers was 49.5% calculated as the secondary ether formed. When 150 cc. of 75% acid was used the crude ethyl ether in the product amounted to 38%. No ethers were formed when a 15% solution of sodium hydrogen sulfate was used. The products in all cases contained the three possible ethers, the mixed ether predominating. This fact is in accord with the labilities of the bonds involved.

Isobutyl Ethyl Ether.—This ether was prepared from isobutyl alcohol (b. p. 107.9), sodium and ethyl bromide. The yield of purified ether was 66%.

Preparation of Isopropyl Ethyl Ether.—In the study of the formation of this ether from the alcohols and sulfuric acid the following results were obtained.

When 200 cc. of isopropyl alcohol, 300 cc. of ethyl alcohol and 534 cc. of sulfuric acid (75%) were used the yield of ethers formed was 77.5% calculated as isopropyl ethyl ether. The mixture on fractionation was shown to contain 34% diethyl ether and 61% isopropyl ethyl ether. A series of experiments showed that the yield of ethers decreased with decrease in the strength of the acid, but that the proportion of mixed ether increased.

When 25 cc. of each alcohol was slowly distilled with 200 cc. of 50% acid, the yield of the product, which was shown to be chiefly the mixed ether, was 33.8%.

The isopropyl ethyl ether boiled at 53–54° and had the density 0.720_4^{25}.

In all the preparations the reaction was very slow. Fourteen hours were required to complete the experiments noted above.

Preparation of *Tert.*-butyl Acetate.—This compound was prepared by a number of different methods. The method described in the literature[12] furnishes a yield of impure ester of 45% of the theoretical.

When 10 cc. of *tert.*-butyl alcohol, 14 cc. of acetic acid and 10 cc. of 15% sulfuric acid were used, the yield of ester was 24%.

When 100 cc. of the alcohol, 78.5 cc. of acetic acid and 100 cc. of an aqueous solution of sodium hydrogen sulfate were used, the yield of ester before purification was 65%.

Acetic anhydride gave better results. The ester can be prepared conveniently from commercial 90% *tert.*-butyl alcohol as follows: 100 cc. of the alcohol, 100 cc. of acetic anhydride and 1 g. of zinc dust are refluxed for two hours. The product is dis-

[12] Kondakow, *Bull. soc. chim.*, [3] **7**, 583 (1892).

tilled and the portion boiling below 98° is refluxed with 50 cc. of acetic anhydride. The yield (94%) was 114 cc. of the ester which boiled at 97.8°. Equally good results were obtained when zinc was replaced by magnesium.

Significant results using anhydrous *tert.*-butyl alcohol were as follows: 10 cc. of the alcohol and 10 cc. of the anhydride reacted under the influence of 0.004 g. of anhydrous zinc chloride. On standing for twelve hours at room temperature, or by refluxing for one hour, the yield of crude ester was the theoretical.

The preparation of the ester from the alcohol and acetyl chloride furnished an explanation of the behavior of tertiary alcohols with acyl chlorides. It has been concluded in the past that tertiary alcohols behave abnormally in their reactions with acyl chlorides in that tertiary halides and acetic acid are formed instead of an ester and hydrochloric acid.

In the presence of a molecular quantity of dimethylaniline, a 98% yield of the ester was obtained. In the absence of the amine and when heated to boiling for ten minutes, 50% ester and 50% chloride were formed. When the temperature was kept below 20°, a quantitative yield of the chloride was formed.

These facts show that the primary reaction between the alcohol and the acyl chloride is the formation of the ester. The latter subsequently reacts with the hydrochloric acid and is converted into the butyl chloride. The ester is rapidly converted into the chloride by concentrated hydrochloric acid.

When *tert.*-butyl acetate (5 cc.) was refluxed with methyl alcohol (1 cc.) and 2 drops of concentrated sulfuric acid, the chief product was methyl acetate.

Preparation of *Tert.*-butyl Benzoate.—Twenty cc. of anhydrous *tert.*-butyl alcohol, 24.4 cc. of pyridine and 16.8 cc. of benzoyl chloride were mixed. Heat was evolved and white crystals separated. The next day the mixture was treated with water and the oil dried and distilled at 2 mm. pressure. The yield of the ester was 80%. Its physical properties are given in Table II.

The compound decomposed completely into isobutylene and benzoic acid when distilled at atmospheric pressure. Dilute sulfuric and hydrochloric acids hydrolyze it rapidly; it appears to be quite stable toward a solution of sodium hydroxide.

TABLE II

PROPERTIES OF CERTAIN MIXED ETHERS AND COMPOUNDS CONTAINING THE *Tert.*-BUTYL RADICAL

The compounds marked with an asterisk, some of the indexes of refraction, and the minimum boiling mixtures with water are reported for the first time.

Compound	Boiling point, °C., at 760 mm. (corr.)	Minimum b. p. with water, °C., at 760 mm. (corr.)	d_4^{25}	n_D^{25}
Tert.-$C_4H_9OCH_3$	55.2	51	0.7354	1.3667
Tert.-$C_4H_9OC_2H_5$	73.1	64	.7364	1.3728
**Tert.*-C_4H_9O-*n*-C_3H_7	97.4	81	.7472	1.3830
Tert.-C_4H_9O-*n*-C_4H_9	124	88	.758	1.3928
Tert.-C_4H_9O-*iso*-C_3H_7	87.6	71	.7365	1.3773
**Tert.*-$C_4H_9OC_2H_4OC_2H_5(\beta)$	147	94	.829	1.4170
**Sec.*-$C_4H_9OC_2H_5$	81.2	71	.7377	1.3753
Iso-$C_4H_9OC_2H_5$	81.1	69	.7323	1.3739
n-$C_4H_9OC_2H_5$	92.3	75	.7447	1.3798
Tert.-C_4H_9Cl	50.7	49	.8370	1.3828
Tert.-$C_4H_9OOCCH_3$	97.8	76	.8593	1.3838
**Tert.*-$C_4H_9OOCC_6H_5$	96 (2 mm.)	..	.9928	1.4896

Chemical Reactions of the Mixed Ethers with Acetic Acid.—None of the highly purified ethers reacted with glacial acetic acid at room temperature or when heated at 100° for forty-eight hours. The reported formation of the acetate from *tert.*-butyl ethyl ether was no doubt due to the presence of the alcohol in the ether used. In the presence of a trace of sulfuric acid this ether was converted almost quantitatively by acetic acid into ethyl acetate and *tert.*-butyl alcohol. The latter may not have been the primary products of the reaction since it was shown, as stated above, that *tert.*-butyl acetate is converted by methyl alcohol in the presence of sulfuric acid into methyl acetate and the tertiary alcohol.

At room temperature there was no reaction between any of the ethers and acetic acid in the presence of zinc chloride.

With Acetyl Chloride.—There was no reaction between the ethers and acetyl chloride in the absence of a catalyst. All the mixed ethers reacted slowly with acetyl chloride at room temperature in the presence of anhydrous zinc chloride.

When *n*-butyl ethyl ether was used and the reactants were allowed to stand for twenty-one days in a sealed tube, the products obtained were separated and determined. The reaction which led to the formation of ethyl acetate and normal butyl chloride took place to the extent of 33.6% when measured by the amount of the former product and 36.6% by the amount of the latter. The reaction by which *n*-butyl acetate and ethyl chloride were formed was found to be 58.3% from the former and 58.6% from the latter. At 60° the reactions by which ethyl acetate and *n*-butyl acetate were formed took place to the extent of 23 and 76%, respectively.

When isobutyl ethyl ether was allowed to stand with acetyl chloride and zinc chloride at room temperature for sixteen days, the ethyl acetate reaction took place to the extent of 22.8% (from ethyl acetate formed) and 21% (from *n*-butyl chloride) and the *n*-butyl acetate reaction 65% (from acetate) and 64% (from ethyl chloride).

When *sec.*-butyl ethyl ether was used the products, after twelve days, were as follows: 95.6% ethyl acetate and 76.5% secondary butyl chloride.

Tert.-butyl ethyl ether reacted rapidly at room temperature. After standing overnight the theoretical yield of ethyl acetate and *tert.*-butyl chloride was obtained. The same result was obtained when the mixture was heated for ten minutes.

With Benzoyl Chloride.—All the ethers reacted at room temperature with benzoyl chloride in the presence of zinc chloride. The reaction was slower than with acetyl chloride. Analogous products were obtained—*n*-butyl ethyl ether gave 86% *n*-butyl benzoate, after standing for sixty-one days; the isobutyl ether 62.5% isobutyl benzoate; the *sec.*-butyl ether 98% *sec.*-butyl chloride and the *tert.*-butyl ethyl ether, on standing for twelve hours, gave 99% of *tert.*-butyl chloride and ethyl benzoate.

With Acetic Anhydride.—The ethers did not react at room temperature. In the presence of zinc chloride the results were as follows: *n*-butyl ethyl ether in sixty-two days, 13% each of butyl acetate and ethyl acetate; the isobutyl ether in sixty-two days, 8% of the two acetates; the *sec.*-butyl ether in forty-three days, 23%; *tert.*-butyl ethyl ether, overnight, 82%. In all cases the two acetates were formed in equivalent amounts.

Zinc dust can be used instead of zinc chloride. When equivalent quantities of *tert.*-butyl ethyl ether and acetic anhydride were refluxed with zinc dust for two hours, a quantitative yield of the two esters was obtained.

Zinc Chloride as Catalyst.—Zinc chloride does not act as a true catalyst in the reaction described above. When acetic acid, acetyl chloride, or acetic anhydride was used, the chloride at first dissolved and later zinc acetate separated in crystalline form. The salt was identified by its melting point, 342.5–343° (uncorr.) and by its properties. The reactions brought about by zinc chloride took place when zinc acetate or magnesium dust was used.

At room temperature zinc chloride does not decompose the mixed ethers, but forms a compound with them. When a solution of zinc chloride in *tert.*-butyl methyl ether which had stood for eighty-one days was opened there was no evidence of the presence of an unsaturated hydrocarbon. When the excess of the ether was removed an oil was obtained which decomposed at 80° and yielded a gas which showed the properties of methyl chloride. When the evolution of gas ceased, the product was heated to 165°; at this temperature there was a second evolution of gas, which proved to be an unsaturated hydrocarbon. When some of the liquid obtained by heating the addition product to 165° was treated with concentrated hydrochloric acid, *tert.*-butyl chloride was formed.

Summary

1. The results of the previous study of the relative reactivities of the hydroxyl group and the hydrogen of this group in the three classes of alcohols have been utilized in devising new and improved methods for the preparation of certain mixed ethers.

2. Mixed ethers which contain the *tert.*-butyl radical and a methyl, ethyl, *n*-propyl, *n*-butyl or isopropyl radical can be prepared conveniently with satisfactory yields, when the two alcohols are heated with a 15% aqueous solution of sulfuric acid or of sodium hydrogen sulfate.

3. In order to prepare ethers containing a secondary and a primary radical, the strength of the acid to effect the reaction must be 50% or greater. In all cases the three possible ethers are formed, the mixed ether being produced in the largest amount.

4. The results indicate that the mechanism of the formation of ethers with the use of sulfuric acid does not involve the intermediate formation of an alkyl sulfuric acid. An addition product of an alcohol and sulfuric acid is probably the active material involved.

5. A number of mixed ethers have been prepared in a very pure condition and their physical constants determined.

6. The behavior of a number of mixed ethers with hydrochloric acid, sulfuric acid, acetic acid, acetyl choride, benzoyl chloride and acetic anhydride has been studied. The results obtained are in accord with labilities of the bonds involved, as determined by rates of reactions.

7. *Tert.*-butyl acetate and benzoate have been prepared by new and improved methods and their behavior studied.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

PARA-HALOGEN-PHENACYL ESTERS OF THE NORMAL FATTY ACIDS

BY CARRIE GUTMAN MOSES AND E. EMMET REID

RECEIVED FEBRUARY 10, 1932 PUBLISHED MAY 7, 1932

A number of these esters were prepared by Judefind and Reid[1] and others by Hann, Reid and Jamieson.[2] It has seemed desirable to fill the gaps in the series both for the sake of completeness and to study the relations of the melting points of the various derivatives to each other.

It is well known that the melting points of the normal hydrocarbons and of their simple derivatives show alternations as we go from one member to the next in a series. It has recently been found by Malone and Reid[3] that the melting points of the 3,5-dinitrobenzoates of the normal alcohols show the same phenomenon. It was of interest to see whether this would also be found to be true with these derivatives of the acids.

In order to have strictly comparable data, all of the derivatives have been fully prepared whether they had been made previously or not. On recrystallization most of the esters appear as brilliant white plate-like

TABLE I

MELTING POINTS OF THE *p*-HALOGEN-PHENACYL ESTERS OF THE NORMAL FATTY ACIDS

	Chloro, °C.		Bromo, °C.			Iodo, °C.	
Formic	128.0		135.2			163.0	
Acetic	72.4	67.2[a]	86.0	85.0[a]		117.0	114.0[a]
Propionic	98.2		63.4	59.0[a]		98.0	94.9[a]
Butyric	55.0		63.0	63.2[a]		81.5	81.4[a]
Valeric	97.8		75.0	63.6[a]		81.0	78.6[a]
Caproic	62.0		72.0	71.6[a]		84.0	81.5[a]
Heptoic	65.0		72.0			78.8	
Caprylic	63.0		67.4	65.5[a]		79.2	77.0[a]
Pelargonic	59.0		68.5			77.0	
Capric	61.6		67.0	66.0[a]		82.0	80.0[a]
Undecylic	60.2		68.2			81.8	
Lauric	70.0	70.0[b]	76.0	76.0[b]		85.8	
Tridecylic	67.0		75.0			88.5	
Myristic	76.0	76.0[b]	81.0	81.0[b]		89.8	
Pentadecylic	74.0		77.2			93.0	
Palmitic	82.0	82.0[b]	86.0	81.5[a]	86.0[b]	94.2	90.0[a]
Margaric	78.8		82.6	78.2[a]		92.0	88.8[a]
Stearic	86.0	86.0[b]	90.0	78.5[a]	90.0[b]	97.2	90.5[a]

[a] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

[b] Hann, Reid and Jamieson, *ibid.*, **52**, 818 (1930).

[1] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

[2] Hann, Reid and Jamieson, *ibid.*, **52**, 818 (1930).

[3] Malone and Reid, *ibid.*, **51**, 3424 (1929).

crystals. The acetic esters are tinged with yellow which becomes more pronounced with exposure to the light. The formic esters suffer this change more quickly and melt with decomposition.

The melting points are given in Table I and are plotted in the figure.

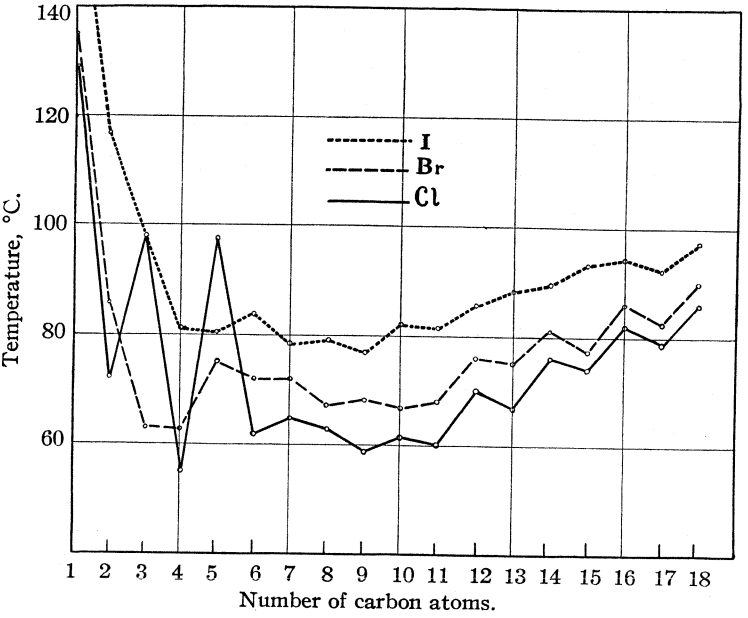


Fig. 1.

The chloro series shows well-defined alternations, the swings being very wide for the first six compounds. At the eighth compound there is a reversal of the alternation, the odd-numbered compounds melting higher up to that point and after it the even. In the bromo series this reversal takes place at the eleventh member. In the iodo series there is a well-defined alternation from five to twelve and again from fifteen to eighteen but in the reversed sense. In this series the butyric and valeric esters melt at nearly the same point while in the bromo series this is true of the propionic and butyric.

It seemed of interest to compare the melting points of the *p*-bromophenacyl derivatives from mixtures of palmitic and stearic acids with that of the margaric acid derivative. The results are given in Table II.

The derivative from 2:1 mixture does not change its melting point on recrystallization. That of 1:2 derivative approximates that of the margaric acid derivative, 82.6°, but is not sharp and is raised on recrystallization. The appearance of the derivative from the mixture is very different from one of the pure acids.

TABLE II

MELTING POINTS OF *p*-BROMOPHENACYL ESTERS OF PALMITIC AND STEARIC ACIDS AND THEIR MIXTURES

Palmitic	Stearic	Crude, °C.	Recryst., °C.
1	0		86.0
0	1		90.0
1	1	79.0	80.4
1	2	82.5	83.8
2	1	80.6	80.6

Experimental

The methods used were substantially those already described in the papers quoted. The one uniformly giving best results was found to be the neutralization of a weighed amount of the acid with slightly less than the theoretical amount of sodium alcoholate, heating (the higher acids) until all was in solution, testing for acidity with slightly moistened litmus paper (the solution must be slightly acid) and, if necessary, adding a minute quantity of the acid itself or, in case of the higher acids, hydrochloric acid. The alcoholate was made by adding three grams of sodium to one liter of 95% alcohol. An amount of the reagent calculated for the quantity of base used was then introduced and the whole refluxed for an hour. With the lower acids a small quantity of water was required but the esters of the higher acids precipitated from the alcoholic solution on cooling under the tap.

The precipitate was filtered rapidly with suction, well washed with cold alcohol, dilute alcohol and water and then dried between filter paper for at least twenty-four hours, after which the melting point was taken and the compound recrystallized. This procedure was repeated until a constant melting point was obtained. The melting points were determined in a Thiele tube filled with mineral oil, using a thermometer corrected by the Bureau of Standards.

Summary

The para chloro, bromo and iodophenacyl esters of the normal acids from acetic to stearic have been prepared and their melting points compared.

Alternation in the melting points appears in all these series.

BALTIMORE, MARYLAND

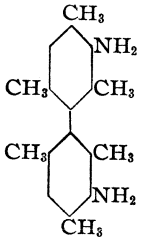
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL. XXI. RESOLUTION OF 2,4,6,2',4',6'-HEXACHLORO-3,3'-DICARBOXYDIPHENYL[1,2]

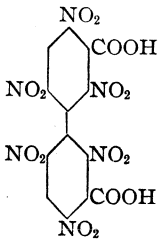
BY JULIUS WHITE AND ROGER ADAMS

RECEIVED FEBRUARY 11, 1932 PUBLISHED MAY 7, 1932

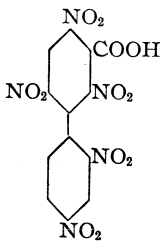
In previous papers two compounds have been described in which all four groups in the 2,2',6,6' and one compound in which three groups in the 2,2',6 positions in diphenyl have been substituted by the same groups. These are 2,4,6,2',4',6'-hexamethyl-3,3'-diaminodiphenyl (I), 2,4,6,-2',4',6'-hexanitro-3,3'-dicarboxydiphenyl (II) and 2,4,6,2',4'-pentanitro-3-carboxydiphenyl (III).[3] Since each ring in itself is asymmetrically substituted in these compounds, enantiomorphic forms of each are capable of existence and were actually produced in the laboratory.



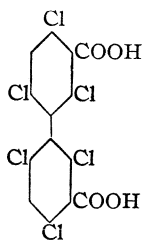
I



II



III



IV

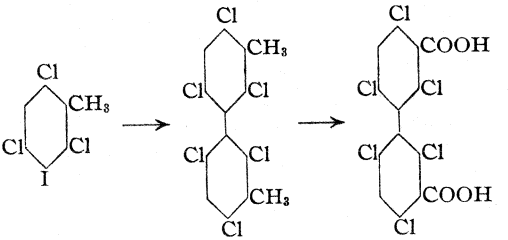
Another example of this type is described in this communication in which the chlorine atom is present in the positions adjacent to the diphenyl linkage. The substance prepared was 2,4,6,2',4',6'-hexachloro-3,3'-dicarboxydiphenyl (IV). It was resolved through the brucine salt. The *d*-active compound was stable to racemization in boiling alcohol, glacial acetic acid and, as the sodium salt, in boiling water.

The compound was synthesized by starting with trichloro-*m*-toluidine and converting it first to 2,4,6-trichloro-3-iodotoluene (V). By means of copper powder 2,4,6,2',4',6'-hexachloro-3,3'-dimethyldiphenyl (VI) was produced. By means of a mixture of potassium permanganate and nitric acid, in a sealed tube at 180°, 2,4,6,2',4',6'-hexachloro-3,3'-dicarboxydiphenyl resulted.

[1] For the last papers in this field see: Woodruff and Adams, *ibid.*, **54**, 1977 (1932); Hill and Adams, *ibid.*, **53**, 3453 (1931); Bock and Adams, *ibid.*, **53**, 3519 (1931).

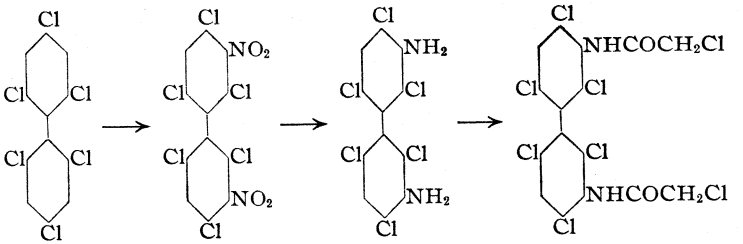
[2] This communication is a portion of an abstract of a thesis submitted by Julius White in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Moyer and Adams, THIS JOURNAL, **51**, 630 (1929); Bock, Moyer and Adams, *ibid.*, **52**, 2054 (1930); Stearns and Adams, *ibid.*, **52**, 2070 (1930).



V VI IV

Before the above procedure was developed a number of interesting but unsuccessful experiments were performed to obtain compounds containing a properly substituted chlorinated diphenyl with salt-forming groups. In particular 2,4,6,2′,4′,6′-hexachlorodiphenyl (VII) was readily nitrated to the 3,3′-dinitro-2,4,6,2′,4′,6′-hexachlorodiphenyl (VIII) and this in turn was reduced to the corresponding diamine (IX).



VII VIII IX X

The diamine, on account of the lack of basicity of the amino group, could not be converted into stable salts. To introduce salt-forming groups the diamine was converted to the di-chloroacetamido compound (X) and then this product was treated with ammonia and amines to replace the halogens. No well-characterized compounds were obtained from the di-chloroacetamido compound.

Experimental

2,4,6-Trichloro-*m*-toluidine.—The general method of Bures and Rubes[4] was employed. To 90 g. of *m*-toluidine in a 3-liter round-bottomed flask connected with a mechanical stirrer and a reflux condenser was added cautiously 1 liter of acetic anhydride. A continuous stream of chlorine was passed in. The reaction mixture became warm but no external cooling was necessary. At the end of six to eight hours the reaction was complete as indicated by the reaction mixture becoming cold and a portion of the chlorinated product separating out. Water was slowly and carefully added to decompose the excess of acetic anhydride and to precipitate completely the product from solution. It was purified from hot ethyl alcohol and melted at 180–181°. To this acetylated derivative 250 g. of 50% sulfuric acid was added and the trichloro-*m*-toluidine was steam distilled. No recrystallization was necessary, m. p. 77–78°.

1-Iodo-2,4,6-trichloro-3-methylbenzene.—A solution of 65 g. of trichloro-*m*-toluidine[4] in 400 cc. of concentrated sulfuric acid was cooled to 15–20°, stirred, and

[4] Bures and Rubes, *Coll. Czechoslov. Chem. Communications*, **1**, 648 (1929).

32.5 g. of solid sodium nitrite was slowly added. The mixture was stirred for one hour after addition of the nitrite and then carefully poured into a very large excess of cracked ice. A solution of 65 g. of potassium iodide dissolved in 125 cc. of water was now slowly added with stirring. The solution was warmed to 40° until no more oxides of nitrogen were liberated and the excess of iodine was removed by the addition of sodium bisulfite. The crude iodo product was recrystallized from acetone as white crystals, m. p. 95–97°.

Anal. Calcd. for $C_7H_4Cl_3I$: Cl + I, 72.3. Found: Cl + I, 72.12.

2,4,6,2′,4′,6′-Hexachloro-3,3-dimethyldiphenyl.—A mixture of 50 g. of the trichloroiodotoluene and 50 g. of copper bronze was heated on an oil-bath for three hours at 235–250°. The mixture was cooled and extracted with hot ethyl alcohol several times. Crystals of hexachlorodimethyldiphenyl separated on cooling and could be recrystallized from alcohol as white crystals, m. p. 119–120°.

Anal. Calcd. (Parr Bomb): Cl, 54.75. Found: Cl, 54.92.

2,4,6,2′,4′,6′-Hexachloro-3,3′-dicarboxydiphenyl.—The hexachlorodimethyldiphenyl was oxidized to the hexachlorodicarboxydiphenyl by means of potassium permanganate and nitric acid (sp. gr. 1.15–1.20). The general method of Rupp[5] was used. A mixture of 5 g. of hexachlorodimethyldiphenyl, 3.2 g. of solid potassium permanganate, 23 cc. of concentrated nitric acid and 25 cc. of water was placed in a Carius tube and heated on an oil-bath at 175–185° for eight hours. After the tube was cooled, the reaction mixture was treated with water and the precipitate filtered. The acid was dissolved in very dilute sodium hydroxide and reprecipitated with dilute hydrochloric acid. It was further purified by recrystallization from a mixture of ethyl acetate and petroleum ether; white crystals, m. p. 318–320°.

Anal. Calcd. for $C_{14}H_4O_4Cl_6$: C, 38.4; H, 0.89. Found: C, 38.76; H, 0.83.

Resolution of 2,4,6,2′,4′,6′-Hexachloro-3,3′-dicarboxydiphenyl.—To 450 cc. of anhydrous ethyl acetate containing 5.384 g. (0.0136 mole) of anhydrous *l*-brucine was added 3.0675 g. (0.0068 mole) of hexachlorodicarboxydiphenyl dissolved in 350 cc. of anhydrous ethyl acetate. An immediate precipitate resulted. This was allowed to stand overnight. It was then filtered and washed with a small amount of anhydrous ethyl acetate. The weight of the salt was 3.4 g. melting at 209°.

Rotation. 0.2050 g. made up to 15 cc. with ethyl alcohol (95%) at 25° gave α_D −0.20°; $l = 2$; $[\alpha]_D^{25}$ −7.3°. The salt was purified by washing with boiling ethyl acetate but with no change in melting point or rotation.

Anal. Calcd. for $C_{60}H_{56}Cl_6N_4O_{12}$: C, 56.66; H, 4.53; Cl, 17.08; N, 4.49. Found: C, 56.93; H, 4.68; Cl, 16.79; N, 4.58.

The mother liquor was evaporated to 100 cc. and allowed to stand overnight. More salt separated. It weighed 1.2 g. The mother liquor was further concentrated *in vacuo* to 50 cc. and allowed to stand overnight. The weight of this last fraction of salt was 3.7 g., m. p. 206–210°.

Rotation. 0.2050 g. made up to 15 cc. with ethyl alcohol (95%) at 25° gave α_D −0.49°; $l = 2$; $[\alpha]_D^{25}$ −15.5°. The salt was recrystallized from a mixture of ethyl acetate and petroleum ether, melting again at 206–210° and with no change in rotation.

Anal. Calcd. for $C_{60}H_{56}Cl_6N_4O_{12}$: C, 56.66; H, 4.53. Found: C, 57.13; H, 4.74.

***d*-2,4,6,2′,4′,6′-Hexachloro-3,3′-dicarboxydiphenyl.**—The pure dibrucine salt was dissolved in chloroform and shaken with dilute hydrochloric acid several times. The chloroform layer was then separated and shaken with dilute sodium hydroxide. The

[5] Rupp, *Ber.*, **29**, 1625 (1896).

sodium hydroxide layer was separated and treated with dilute hydrochloric acid. The acid which precipitated out was filtered off and recrystallized from a mixture of ethyl acetate and petroleum ether. It was found to be brucine-free and melted at 293–294°. Further recrystallization did not change the melting point.

Rotation. 0.4442 g. made up to 15 cc. in ethyl alcohol (95%) at 25° gave α_D +0.10; $l = 2$; $[\alpha]_D^{25}$ +1.7°. The acid was again recrystallized and the rotation taken. 0.3234 g. made up to 15 cc. in ethyl alcohol (95%) at 25° gave α_D +0.08°; $l = 2$; $[\alpha]_D^{25}$ +1.8.

Further recrystallization did not alter the rotation.

Anal. Calcd. for $C_{14}H_4O_4Cl_6$: C, 38.4; H, 0.89. Found: C, 38.79; H, 1.08.

***l*-2,4,6,2′,4′,6′-Hexachloro-3,3′-dicarboxydiphenyl.**—The more soluble salt was hydrolyzed in a manner similar to the less soluble salt. The acid thus obtained was recrystallized from a mixture of ordinary ethyl acetate and petroleum ether, and melted at 292–293°.

Rotation. 0.4425 g. made up to 15 cc. in ethyl alcohol at 25° gave α_D −0.09°; $l = 2$; $[\alpha]_D^{25}$ −1.52°.

The acid was recrystallized and the rotation again taken.

0.4204 g. made up to 15 cc. in ethyl alcohol (95%) gave α_D 0.096°; $l = 2$; $[\alpha]_D^{25}$ −1.7°.

Racemization Experiments

1. A sample of the *d*-acid was dissolved in ordinary ethyl alcohol and refluxed in a flask with a ground-glass joint for eight hours. No change in rotation was observed.

Rotation. 0.4464 g. made up to 15 cc. with ethyl alcohol at 25° gave α_D +0.11; $l = 2$; $[\alpha]_D^{25}$ +1.8°.

2. A second sample of the *d*-acid was dissolved in glacial acetic acid and the rotation taken. 0.4520 g. of acid in 15 cc. of glacial acetic acid at 25° gave α_D +0.18; $l = 2$; $[\alpha]_D^{25}$ +3.01.

3. After refluxing for periods of two and six hours, respectively, no change in rotation occurred.

4. 0.4005 g. of acid was exactly neutralized with 36.3 cc. of 0.0554 *N* sodium hydroxide and the solution concentrated *in vacuo* to dryness. This was made up with water to 15 cc. of 25° and the rotation taken. α_D +0.22; $l = 2$; $[\alpha]_D^{25}$ +4.01 based on the sodium salt of 0.4005 g. of acid.

The water solution was then refluxed at intervals of three hours, two hours and nine hours. No change in rotation was observed.

2,4,6,2′,4′,6′-Hexachloro-3,3′-dinitrodiphenyl.—To 60 g. of fuming nitric acid (sp. gr., 1.50) cooled in an ice-bath was added slowly with rapid stirring 10 g. of hexachlorodiphenyl.[6] The temperature was maintained at 0° and stirring continued for one hour after all of the hexachlorodiphenyl had been added. The mixture was poured into cracked ice and the precipitate was purified by recrystallization from hot alcohol, m. p. 230–231°.

Anal. Calcd. for $C_{12}H_2Cl_6N_2O_4$ (Parr Bomb): Cl, 47.23. Found: Cl, 47.38.

2,4,6,2′,4′,6′-Hexachloro-3,3′-diaminodiphenyl.—To a solution of 2 g. of 2,4,6,-2′,4′,6′-hexachloro-3,3′-dinitrodiphenyl in 50 g. of glacial acetic acid and 5 g. of water was added gradually with constant stirring 5 g. of zinc dust. The mixture was allowed to heat up from the heat of reaction (about 80°). It was then heated on a water-bath for fifteen minutes to complete the reaction. The mixture was diluted with water and filtered. The amine was separated from the excess of zinc by several extractions with

[6] Ullmann, *Ann.*, **332**, 40 (1904).

hot 95% ethyl alcohol. It was purified by recrystallization from hot 60–70° petroleum ether; white crystals, m. p. 167.5–168.5°.

Anal. Calcd. for $C_{12}H_6Cl_6N_2$ (Parr Bomb): Cl, 54.50. Found: Cl, 54.88.

2,4,6,2′,4′,6′-Hexachloro-3,3′-chloroacetaminodiphenyl.—A mixture of 2 g. of the hexachlorodiaminodiphenyl and an excess of chloroacetyl chloride was refluxed for several hours on a steam cone. The mixture was then cooled and the excess of chloroacetyl chloride was decomposed with cracked ice. The product was recrystallized from 70–80° petroleum ether as white crystals, m. p. 125–126°.

Anal. Calcd. for $C_{16}H_9Cl_6N_2O_2$ (Parr Bomb): Cl, 52.2. Found: Cl, 52.3.

Attempts to condense hexachlorodiaminodiphenyl with *d*-camphorsulfonic acid and oxymethylenecamphor, respectively, proved unsuccessful.

Summary

1. 2,4,6,2′,4′,6′-Hexachloro-3,3′-dicarboxydiphenyl was prepared by the condensation of 1-iodo-2,4,6-trichloro-3-methylbenzene with copper and oxidation of the product.

2. The product was resolved through the brucine salt. The active forms were stable to ordinary methods of racemization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE ACTION OF MERCURY ON ORGANIC IODIDES. I. THE FORMATION OF METHYLMERCURIC IODIDE AND BENZYLMERCURIC IODIDE[1]

BY J. LEWIS MAYNARD

RECEIVED FEBRUARY 12, 1932 PUBLISHED MAY 7, 1932

Introduction

For over eighty years it has been known that when mercury is allowed to stand in the sunlight with methyl or ethyl iodide, reactions occur with the formation of organomercuric iodides, RHgI, and certain gaseous products.[2] In addition to the instances cited, the direct action of mercury with organic iodides has been noted only in the cases of allyl iodide,[3] methylene iodide and iodoform,[4] and propargyl iodide.[5] With the higher saturated alkyl iodides it is possible that a very slow reaction with mercury takes place, but no accurate data are available.[6] Up to the present time,

[1] A part of this material has been presented in a thesis submitted to the University of Minnesota.

[2] Frankland, *J. Chem. Soc.*, **3**, 322 (1851); *Ann.*, **111**, 59 (1859); Strecker, *ibid.*, **92**, 76 (1854).

[3] Zinin, *ibid.*, **96**, 363 (1855).

[4] Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); **39**, 485 (1881); **41**, 360 (1882).

[5] Henry, *Ber.*, **17**, 1132 (1884).

[6] Whitmore, "Organic Compounds of Mercury," A. C. S. Monograph Series, The Chemical Catalog Co., New York, 1921, p. 26.

no other halogen alkyls or any aryl halides have been found to react with mercury to give organomercuric halides.

Preliminary Observations.—The preparation of a large quantity of methylmercuric iodide, CH_3HgI, was carried out by the action of mercury on methyl iodide in the sunlight. During the course of this work it was noted that in each batch there was a lag of from three to ten hours before the presence of methylmercuric iodide could be detected in the reaction mixture. The first observable mercury compound to be formed was invariably found to be mercurous iodide, its presence being detected by the appearance of green specks on the surface of the layer of mercury. The formation of this compound resulted from the action of an excess of mercury on iodine liberated photochemically from methyl iodide. After a lapse of time of a few minutes, methylmercuric iodide in steadily increasing concentration was found in solution in the methyl iodide. A reason was sought for the failure of the organomercuric iodide to appear until after the formation of mercurous iodide.

Discussion and Further Observations.—From the observed behavior of a mixture of mercury and methyl iodide it was concluded that mercurous iodide facilitated the formation of methylmercuric iodide.[7] Acceptance of this conclusion demanded that there be no lag in the formation of methylmercuric iodide on exposure of a mixture of mercury, mercurous iodide and methyl iodide to the sunlight. This proved to be the case, for, after a few minutes of exposure of such a mixture, methylmercuric iodide was found to be present. Since the mixture did not react in the dark, and since pure mercurous iodide alone reacted with methyl iodide in the light in the absence of an excess of mercury, it was decided that the mercury necessary for the reaction in either case was produced by the photochemical decomposition of mercurous iodide. Thus: $Hg_2I_2 \longrightarrow Hg + HgI_2$. The metal formed in this manner was in a finely divided condition.

The conclusion reached was supported by further experimental evidence. It must be noted at this point that the course of the reactions between mercury and methyl iodide was the same whether the source of light was the sun, a mercury vapor lamp or a carbon arc. In this study the arc was selected as the most convenient source of illumination. Light from this source brought about the liberation of iodine from methyl iodide, and, with an excess of massive mercury present, the formation of mercurous iodide took place. This was followed shortly by the formation of methylmercuric iodide. If, however, the photochemical decomposition of the methyl iodide was prevented by passing the light through a screen of cod liver oil, neither mercurous iodide nor methylmercuric iodide was formed during an exposure of seventy-two hours. It was found also that the photochemical decomposition of methyl iodide was not necessary for the

[7] *Cf.* Maynard and Howard, *J. Chem. Soc.*, **123**, 963 (1923).

reaction between mercury and the alkyl iodide, because a mixture of the latter with mercurous iodide reacted behind a screen of cod liver oil to form the organomercuric iodide. Mercurous iodide was photochemically decomposed in the shielded system.

Conclusions.—Thus it has been shown that, while the reaction between massive mercury and methyl iodide must be extremely slow, the finely divided metal reacted readily with the alkyl iodide. This was further demonstrated by the fact that finely divided mercury prepared by the action of ammonium hydroxide on mercurous chloride reacted with methyl iodide protected by a screen of cod liver oil. From this experiment it seemed logical to conclude that mercurous iodide functioned solely as a source of supply of finely divided mercury in the reactions previously noted.

The Action of Mercury on Benzyl Iodide.—With a convenient source of finely divided mercury at hand, it has seemed of interest to attempt to broaden the scope of this action between the metal and an organic iodide by its application to other iodides. Benzyl iodide was the first to be selected for this study, and it was found to react readily and completely with finely divided mercury to form benzylmercuric iodide. The latter compound has been prepared previously in a pure condition only by the action of mercuric iodide on mercury dibenzyl.[8]

$$(C_6H_5CH_2)_2Hg + HgI_2 \longrightarrow 2C_6H_5CH_2HgI$$

This organomercuric iodide has proved to be interesting because work now in progress shows that it reacts with acid chlorides, a reaction not previously noted with a compound of the type RHgI. Studies of the action of mercury with other organic iodides are also being made.

Experimental Part

Reaction between Mercury and Methyl Iodide in the Sunlight.—A stoppered Pyrex test-tube containing 10 g. of mercury and 20 g. of methyl iodide was exposed to direct sunlight at a temperature of 30°. Frequent tests over a period of three hours showed an absence of methylmercuric iodide. At the end of this time the first speck of mercurous iodide had appeared on the surface of the mercury. Ten minutes later, evaporation to dryness of the methyl iodide left a small quantity of a slightly yellowish crystalline solid. This was recrystallized from a small volume of alcohol, and was identified as methylmercuric iodide by its melting point of 144°. The experiment was repeated five times, and although the period of lag varied considerably because of the obscuring of the sun by clouds during parts of the exposure, in no case was the presence of methylmercuric iodide detected previous to the appearance of mercurous iodide.

The use of larger quantities of reactants, 45 g. of mercury and 80 g. of methyl iodide, yielded 30.9 g. of methylmercuric iodide after an exposure of one week in a sealed Carius tube. This represented a yield of 80.7% of that calculated for 45 g. of mercury reacting in the following way

$$2Hg + I_2 \longrightarrow Hg_2I_2 \quad (1)$$

$$Hg_2I_2 \longrightarrow HgI_2 + Hg \quad (2)$$

$$Hg + CH_3I \longrightarrow CH_3HgI \quad (3)$$

[8] Wolff, *Ber.*, **46**, 64 (1913).

The iodine appearing in reaction (1) was formed by the photochemical decomposition of methyl iodide. It can be seen that when the mercurous iodide reacted as shown in equation (2) it was regenerated from the mercuric iodide and the excess of massive mercury present. The methylmercuric iodide was obtained from the reaction product by extraction with boiling benzene.

The Action of a Mixture of Mercury, Mercurous Iodide and Methyl Iodide in the Sunlight.—To a solution of 1 g. of iodine in 10 ml. of methyl iodide contained in a Pyrex test-tube there was added 13 g. of mercury. The mixture was shaken vigorously to effect the formation of mercurous iodide, and was then exposed to the sunlight at a temperature of 31°. A sample taken after a five-minute exposure showed methylmercuric iodide to be present in solution in the methyl iodide. The organomercuric iodide was identified by its melting point of 144°.

The Action of Mercurous Iodide on Methyl Iodide in the Sunlight.—A mixture of 5 g. of pure yellow mercurous iodide[9] and 10 ml. of methyl iodide was exposed to direct sunlight at 28° in a stoppered Pyrex test-tube. After a ten-minute exposure methylmercuric iodide was found in solution in the methyl iodide.

Mercury and Methyl Iodide in a Shielded System.—A stoppered clear quartz test-tube containing a mixture of 5 g. of mercury and 10 ml. of methyl iodide was suspended in cod liver oil contained in a square, clear quartz container. This system was then exposed to light from a carbon arc placed 25 cm. from the outer quartz container. The light passed through a 3-mm. layer of cod liver oil and at the end of a seventy-two hour exposure the contents of the test-tube remained unchanged. The temperature was 34°.

Mercurous Iodide and Methyl Iodide in a Shielded System.—A mixture of 10 g. of mercurous iodide and 15 ml. of methyl iodide was placed in a stoppered quartz test-tube shielded by a 3-mm. layer of cod liver oil. At the end of a fifteen-minute exposure to light from the arc, methylmercuric iodide was found in solution in the methyl iodide. The temperature was 34°.

Finely Divided Mercury from Mercurous Chloride.—Mercurous chloride was prepared by precipitating it from a 0.1 *N* solution of mercurous nitrate with dilute hydrochloric acid. The precipitate was washed repeatedly with water, and then added in small portions to a concentrated solution of ammonium hydroxide. Mechanical stirring maintained a fine state of division of the product. The black insoluble material was filtered off, washed with water and then dried at room temperature.

Reaction of the Black Precipitate with Methyl Iodide.—A mixture of 10 g. of the black precipitate prepared in the preceding experiment and 15 ml. of methyl iodide was exposed in the shielded system to light from the arc at a temperature of 34°. At the end of a ten-minute exposure enough methylmercuric iodide was obtained for a melting point determination.

The Preparation of Benzylmercuric Iodide.—To 5 g. of iodine dissolved in 10 ml. of alcohol there was added 30 g. of mercury. The mixture was thoroughly shaken until a dark green product was obtained. This was sucked free from alcohol on a Büchner funnel, and then sealed up with 15 g. of benzyl iodide in a short length of Carius tubing. The tube was exposed to light from the arc for three hours at a temperature of 50°. The reaction product was found to be free from benzyl iodide, for no lachrymatory action was noted on opening the tube. The benzylmercuric iodide was extracted with boiling alcohol. The yield of pure product, melting at 117°, was 26 g. or 94.5% of that calculated for 15 g. of benzyl iodide.

[9] Prepared according to directions given in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1923, Vol. IV, p. 896.

The author wishes to acknowledge with appreciation the kindly advice and criticism given by Dr. William H. Hunter during the course of this investigation.

Summary

1. Methylmercuric iodide is not formed from methyl iodide and mercury on exposure to light until after the appearance of mercurous iodide in the reaction mixture.

2. Finely divided mercury produced by the photochemical decomposition of mercurous iodide enters into reaction readily with methyl iodide to form methylmercuric iodide.

3. The action of mercury with organic iodides to form organomercuric iodides has been extended to benzyl iodide.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PINACOL-PINACOLIN REARRANGEMENT. THE REARRANGEMENT OF UNSYMMETRICAL AROMATIC PINACOLS

BY W. E. BACHMANN

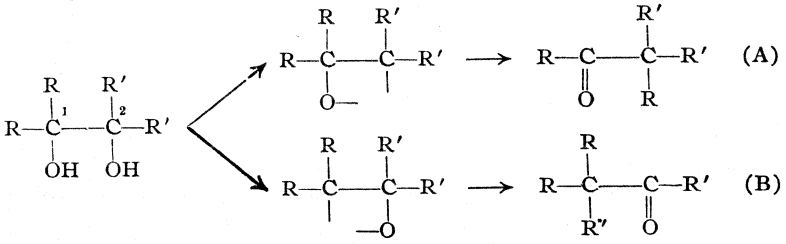
RECEIVED FEBRUARY 23, 1932 PUBLISHED MAY 7, 1932

The rearrangement of symmetrical mixed pinacols of the type RR′(OH)-CC(OH)RR′ has received considerable attention because the reaction offers an excellent method for determining the relative migration aptitudes of groups. The groups R and R′ are in structurally identical positions, and the mode of water elimination from the molecule is therefore immaterial; the principal factor determining the course of the rearrangement is the relative migration aptitudes of the groups. Moreover, it has been shown that in such pinacols each group may be assigned a definite numerical value which represents the migration aptitudes of that group relative to some other group. The most recent series[1] showing the migration aptitudes of a number of groups with respect to the phenyl group taken as unity is the following: anisyl, 70 or more; *p*-tolyl, 15; *p*-biphenyl, 11.5; *p*-isopropylphenyl, 9; *p*-ethylphenyl, 5; *m*-tolyl, 1.95; *p*-fluorophenyl, 1.85; *p*-iodophenyl, 1; phenyl, 1; *p*-bromophenyl, 0.7; *p*-chlorophenyl, 0.66; *m*-methoxyphenyl, 0.2; *o*-tolyl, *o*-bromophenyl and *o*-chlorophenyl, very small. It has further been demonstrated that by means of these values it is possible to calculate the course of rearrangement of a symmetrical pinacol containing two of these groups.

We have now undertaken an investigation to determine whether the same series holds in the rearrangement of unsymmetrical pinacols of the type RR(OH)CC(OH)R′R′. Various investigators have pointed out that in pinacols of this type the nature of the rearrangement depends practi-

[1] Bachmann and Moser, THIS JOURNAL, **54**, 1124 (1932).

cally entirely on the possible mode of elimination of water and not at all on the migration aptitudes of the groups. From the following formulation it is apparent that two isomeric pinacolins are possible, the nature of which depends on the particular H and OH that are eliminated.



Meerwein[2] considered that formation of A is an indication that the OH group attached to C^2 is held more loosely than the OH of C^1. The strength with which the OH group is held to the carbon atom is considered to be dependent upon the nature of the radicals R and R′; if the radicals attached to a particular carbon atom have large affinity capacities, then the OH will be held proportionately loosely to that carbon atom. Formation of A exclusively is, therefore, an indication that R′ has a greater affinity capacity than R. On this basis, the rearrangement offers a method for studying affinity capacities and not migration aptitudes of groups. The view is held by some that the elimination of the hydroxyl group occurs preferentially from that carbon atom to which are attached the groups with the greatest capacity for electron release.[3] Whether these views can be applied also to the unsymmetrical aromatic pinacols is not known because no simple aromatic pinacol of this type has been prepared previous to this investigation. Meerwein studied mixed aliphatic–aromatic pinacols and also the unsymmetrical pinacol containing the phenyl and biphenylene groups and recently Bergmann and Schuchardt[4] rearranged two additional pinacols of this type. In this paper are reported the results obtained by rearranging three unsymmetrical pinacols containing only aryl groups. In each pinacol one carbon atom holds two phenyl groups; to the other carbon atom are attached two anisyl, two *p*-tolyl and two *m*-tolyl groups, respectively, thus offering a comparison of four groups.

In the following table the results obtained previously in the rearrangement of symmetrical pinacols are compared with the results obtained now on unsymmetrical pinacols containing the same groups.

It is immediately apparent that the series representing the relative migration aptitudes of the groups in symmetrical pinacols does not hold for the unsymmetrical pinacols. The series for the latter type of mole-

[2] Meerwein, *Ann.*, **419**, 121 (1919).

[3] "Annual Reports," Vol. 27, 1930, p. 117.

[4] Bergmann and Schuchardt, *Ann.*, **487**, 285 (1931).

TABLE I

MIGRATION OF GROUPS

Groups R,R′	RR′(OH)CC(OH)RR′ Migration, %	RR(OH)CC(OH)R′R′ Migration, %
p-$CH_3OC_6H_4$	98.6	28
C_6H_5	1.4	72
p-$CH_3C_6H_4$	94	49
C_6H_5	6	51
m-$CH_3C_6H_4$	66	50
C_6H_5	34	50

cule may be represented as follows: phenyl, 1; *m*-tolyl, 1; *p*-tolyl, 0.96; anisyl, 0.39. It is especially striking that the anisyl group, which in the symmetrical pinacol migrates nearly exclusively with respect to the phenyl group, migrates to a lesser extent than the phenyl group when these two groups are in the unsymmetrical molecule. If these results are indications of affinity capacities, then the affinity capacities of the groups are: anisyl, 2.57; *p*-tolyl, 1.04; *m*-tolyl, 1; phenyl, 1. It is evident that the value representing the migration aptitude of a group in a certain type of molecule cannot be applied indiscriminately to that group when situated in a different type of molecule.

Work is in progress to determine the relative migration aptitudes of a large number of groups in unsymmetrical pinacols. We wish, moreover, to determine whether it is possible to predict the rearrangement of pinacols containing any two given groups when the relative migration aptitude of each group with respect to a third mutual group is known. Thus, from the results given in Table I, one can calculate that the unsymmetrical pinacols, di-*p*-tolyldianisylglycol, di-*m*-tolyldianisylglycol and di-*p*-tolyldi-*m*-tolylglycol, will rearrange to pinacolins with migration of the groups in the following ratios: *p*-tolyl, 71%; anisyl, 29%; *m*-tolyl, 72%; anisyl, 28%; *p*-tolyl, 49%; *m*-tolyl, 51%. Experiment will show whether these predictions are justified and it is hoped that the results will throw light upon the question of affinity capacities.

At this time we take the opportunity of pointing out certain facts which were apparently overlooked by Bergmann and Schuchardt[4] when they criticized adversely our interpretation of the mechanism of the reduction of aromatic ketones to pinacols by the system magnesium and magnesium iodide.[5] The failure to find benzophenone and benzhydrol on hydrolysis of the reaction mixture does not prove that iodomagnesium ketyl is not initially formed and is not present in small amount. Bergmann and Schuchardt entirely overlooked our formulation of an equilibrium between the iodomagnesium ketyl radicals initially formed and the iodomagnesium pinacolate, 2 $R_2COMgI \rightleftarrows R_2(OMgI)CC(OMgI)R_2$. Obviously, if this equilibrium is nearly entirely in favor of the dimolecular form, then

[5] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927).

only pinacol will be formed on hydrolysis. The situation is analogous to that of diphenyldibiphenyleneethane which in solution dissociates to a very limited extent only into phenylbiphenylene radicals. Bergmann and Schuchardt attribute the color formation in the solution to a small amount of a saturated ketone-magnesium compound, analogous to benzophenone–disodium, $R_2C(ONa)Na$, instead of to the free iodomagnesium ketyl, $R_2\overset{/}{C}OMgI$, which we consider is responsible. In doing so they forget that the solution of pinacolate reacts with iodine and with oxygen at room temperature, that in this reaction the color of the solution is discharged and the ketone is formed; moreover, that even after 90% of the pinacolate has been converted to ketone by this process, the color returns to the solution provided that oxygen and iodine be excluded. They agree with us that the magnesium pinacolate[6] $R_2C(OMgO)R_2$ is capable of dissociation into colored radicals but, curiously enough, they seem to deny this property to the corresponding iodomagnesium pinacolate, $R_2(OMgI)CC(OMgI)R_2$. Finally, Bergmann and Schuchardt have overlooked the fact that by the action of a Grignard reagent such as methylmagnesium iodide on pure pinacol, there is obtained the equilibrium system, iodomagnesium pinacolate $\rightleftarrows$ iodomagnesium ketyl, which exhibits the same color and the same reactions as the system obtained by reduction of the ketone by the binary mixture. It is evident that the reaction between pinacol and Grignard reagent cannot possibly give rise to a saturated ketone-magnesium compound analogous to the ketone-disodium compound.

In this connection it was of interest to see whether the pinacolate of an unsymmetrical pinacol would behave like the symmetrical pinacolates. Accordingly, the pinacolate of *as*-diphenyldianisylglycol was made by adding ethylmagnesium iodide to a solution of the pinacol. The pinacolate solution absorbed iodine and the pinacolate was converted to a mixture of benzophenone and 4,4′-dimethoxybenzophenone. The behavior of the pinacolate is best explained by the following formulations

$$(C_6H_5)_2C(IMgO)-C(C_6H_4OCH_3)_2(OMgI) \rightleftarrows \begin{cases} (C_6H_5)_2C(IMgO)- \xrightarrow{I_2} (C_6H_5)_2C{=}O \\ (CH_3OC_6H_4)_2C(IMgO)- \xrightarrow{I_2} (CH_3OC_6H_4)_2C{=}O \end{cases}$$

The pinacolate obtained from *as*-diphenyldi-*m*-tolylglycol behaved in a similar fashion. It remains to be seen whether it is possible for two symmetrical pinacols, RR(OMgI)CC(OMgI)RR and R′R′(OMgI)CC-

[6] Bergmann and Schuchardt confirm the results we obtained on the composition of the reduction product; by indirect means they showed the presence of magnesium pinacolate, a result that we had obtained by direct analysis.

(OMgI)R'R', to be formed by recombination of the radicals which are formed by dissociation of the pinacolate of an unsymmetrical pinacol, RR(OMgI)CC(OMgI)R'R'.

Experimental

Preparation of the Pinacols.—Acree[7] isolated benzopinacol from the reaction between methyl benzilate and an excess of phenylmagnesium bromide. Meerwein[2] attempted the preparation of *as*-diphenylditolylglycol and *as*-diphenyldianisylglycol by a similar reaction but he reported that the hydroxy ketone and not the glycol resulted. We have employed Acree's method with modifications and were able to synthesize several unsymmetrical pinacols, including those which Meerwein wished to make, although in two cases the hydroxy ketone and not the glycol was isolated.

The general procedure consists in adding a solution of 0.05 g. mole (12.1 g.) of methyl benzilate in 50 cc. of benzene to the Grignard reagent which has been prepared from 0.2 g. mole of the appropriate aryl halide (*p*-bromotoluene, bromoanisole, etc.). After being refluxed for twelve hours the mixture is hydrolyzed with cold ammonium chloride solution. The ether-benzene solution is filtered and evaporated. The crude pinacol is digested with ligroin or alcohol in order to remove oily impurities and the pinacol is filtered off and recrystallized.

Rearrangement of the Pinacols.—The pinacols were rearranged according to the general procedure described in a preceding paper.[1] In the case of the diphenylditolylglycols the rearrangement did not seem to be complete; in these cases the reaction was completed by heating the partially rearranged material with acetic acid and iodine.[5] The mixture of pinacolins was cleaved with potassium hydroxide in the customary manner, $RRRCCOR + KOH \longrightarrow RRRCH + KOOCR$; from the nature of the mixture of acids so obtained it is possible to calculate the extent of migration undergone by each group. Unlike the symmetrical pinacols, the acid which is isolated corresponds to the group which has migrated; thus, the amount of benzoic acid in the mixture indicates the extent of migration of the phenyl group. It is noteworthy how closely the results of several rearrangements agree with one another.

***as*-Diphenyldi-*p*-tolylglycol,**[8] $(C_6H_5)_2(OH)CC(OH)(C_6H_4CH_3)_2$.—The pinacol was recrystallized by adding alcohol to a hot acetone solution of the compound; the pinacol crystallized in colorless needles; yield, 54%; m. p. 167–168° with decomposition. The pinacol is not very soluble in hot alcohol but it dissolves readily in hot acetone and in hot benzene.

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.2; H, 6.6. Found: C, 84.9; H, 6.6.

The mixture of benzoic acid and *p*-toluic acid which was obtained by cleavage of the pinacolins was analyzed by oxidizing the *p*-toluic acid to terephthalic acid[1] which in virtue of its insolubility in water is easily separated from benzoic acid. At the same time a control oxidation was carried out on a synthetic mixture of the two acids of approximately the same composition. The mixtures from two rearrangements were found to have the following compositions by weight: benzoic acid, 47.9%, 47.7%; *p*-toluic acid, 52.1%, 52.3%; average composition by moles: benzoic acid, 50.7%; *p*-toluic acid, 49.3%. Yield of acids: 93%, 94% of the theoretical amount based on the pinacol employed; yield of triarylmethanes: 97%, 98%.

[7] Acree, *Ber.*, **37**, 2761 (1904).

[8] According to Tiffeneau and Lévy, *Bull. soc. chim.*, [4] **49**, 1650 (1931), Erdmann [Thesis, Rostock, 1910] prepared diphenyldi-*p*-tolylglycol but did not study its rearrangement. We did not have Erdmann's thesis at hand and have been unable to find any reference in the literature to the pinacol.

From the mixture of pinacolins which is formed on rearrangement of the pinacol it was possible to isolate one of them in a pure state. Three and one-half grams of pinacol was heated with 10 cc. of acetic acid and 0.5 g. of iodine for ten minutes; the solution was cooled and decolorized with sulfur dioxide. On standing for several days, the solution deposited 1.1 g. of benzoyldi-*p*-tolylphenylmethane, $C_6H_5CO(C_6H_4CH_3)_2C_6H_5$. After recrystallization from acetic acid, the compound melted at 133–135° and was found to be identical with the compound of known structure, which is formed on rearrangement of symmetrical diphenyldi-*p*-tolylglycol. The isomeric pinacolin which was obtained from the mother liquors was difficult to obtain in a pure state.

***as*-Diphenyldi-*m*-tolylglycol,** $(C_6H_5)_2(OH)CC(OH)(C_6H_4CH_3)_2$.—By recrystallization from a mixture of acetone and alcohol the pinacol was obtained in the form of needle-like prisms; yield, 56%; m. p. 156–158° with decomposition. The pinacol is very soluble in hot benzene and in hot acetone, but it is not very soluble in alcohol.

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.2; H, 6.6. Found: C, 85.1; H, 6.6.

The amount of *m*-toluic acid present in the mixture of acids was determined by oxidizing the toluic acid to isophthalic acid which, being little soluble in water, can be readily separated from benzoic acid. Composition by weight of acid mixture (two rearrangements): benzoic acid, 47%, 48%; *m*-toluic acid, 53%, 52%; average composition by moles: benzoic acid, 50.2%; *m*-toluic acid, 49.8%; yield of acids: 90%, 91%; yield of triarylmethanes: 98%, 100%.

***as*-Diphenyldianisylglycol,** $(C_6H_5)_2(OH)CC(OH)(C_6H_4OCH_3)_2$.—Recrystallization of the crude pinacol from a mixture of acetone and alcohol gave colorless needles; yield, 60%; m. p. 166–168°. The pinacol is not very soluble in hot alcohol but it dissolves readily in hot acetone and in hot benzene.

Anal. Calcd. for $C_{28}H_{26}O_4$: C, 78.8; H, 6.1. Found: C, 78.8; H, 6.1.

The mixture of benzoic acid and anisic acid was analyzed by making a methoxyl determination. Composition of acid mixture by weight: benzoic acid, 67.1%, 66.8%; anisic acid, 32.9%, 33.1%; average composition by moles: benzoic acid, 71.6%; anisic acid, 28.4%. Yield of acids: 92%, 97%; yield of triarylmethanes: 102%, 100%. By recrystallization of the mixture of triarylmethanes from alcohol, pure phenyldianisylmethane (m. p. 100°) was isolated.

Diphenyl-*o*-toluylcarbinol, $(C_6H_5)_2(OH)CCOC_6H_4CH_3$.—The action of *o*-tolylmagnesium bromide on methyl benzilate gave an oil from which a small amount of crystals was isolated. These crystals proved to be not the pinacol but the hydroxy ketone, diphenyl-*o*-toluylcarbinol, resulting by the addition of only one molecule of Grignard reagent to the ester group. Recrystallization from acetone and alcohol gave colorless needles; m. p. 116–117°. The compound was split quantitatively into benzhydrol and *o*-toluic acid when it was heated with three parts of a 25% solution of potassium hydroxide in methyl alcohol[9] for five minutes. The carbinol gives an orange-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.1. Found: C, 83.5; H, 6.1.

Diphenyl-α-naphthoylcarbinol, $(C_6H_5)_2(OH)CCOC_{10}H_7$.—The reaction between methyl benzilate and α-naphthylmagnesium bromide gave an oil and several grams of crystals of diphenyl-α-naphthoylcarbinol. Recrystallization from a mixture of acetone and alcohol gave colorless needles; m. p. 156–157°. On being heated with a methyl alcohol solution of potassium hydroxide the carbinol was cleaved quantitatively into benzhydrol and α-naphthoic acid. The carbinol gives a dark brown color with sulfuric acid.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.1; H, 5.4. Found: C, 84.7; H, 5.3.

[9] Acree, *Am. Chem. J.*, 29, 597 (1903).

It is planned to prepare the desired *as*-diphenyl-*o*-tolylglycol and *as*-diphenyldi-α-naphthylglycol by the action of phenylmagnesium bromide on the esters of *o*-tolilic acid and α-naphthilic acid, respectively.

Reaction between Iodomagnesium–diphenyldianisylglycolate and Iodine.—Two grams of *as*-diphenyldianisylglycol was added to a solution of ethylmagnesium iodide in a mixture of ether and benzene; a red color developed but quickly disappeared. The solution absorbed iodine, slowly at room temperature, much more rapidly when heated. The solution was finally warmed with iodine for several hours, then cooled and hydrolyzed. The ether-benzene solution yielded a mixture of benzophenone and 4,4′-dimethoxybenzophenone. The benzophenone was extracted by warming the mixture of ketones with 10 cc. of petroleum ether and filtering the hot mixture. The residual dimethoxybenzophenone after recrystallization from benzene and ligroin melted at 142–144°; yield, 1.0 g. or 87%.

Summary

Three unsymmetrical aromatic pinacols, *as*-diphenyldi-*p*-tolylglycol, *as*-diphenyldi-*m*-tolylglycol and *as*-diphenyldianisylglycol, have been synthesized and rearranged to pinacolins.

These pinacols rearrange to pinacolins with migration of the groups in the following ratios: *p*-tolyl, 49%, phenyl, 51%; *m*-tolyl, 50%, phenyl, 50%; anisyl, 28%, phenyl, 72%.

ANN ARBOR, MICHIGAN

NOTE

Note on the Preparation of Mercury Dibenzyl

BY J. LEWIS MAYNARD

The preparation of this substance in a pure condition and in good yields has heretofore presented certain difficulties. An attempt to prepare it by a reaction of general application to this type of compound failed to yield the desired substance. Benzyl bromide and sodium amalgam do not react to form mercury dibenzyl.[1] It was first prepared by the Grignard reaction between benzylmagnesium chloride and mercuric chloride.[2] The product was slightly impure, as was shown by the melting point of 104°, seven degrees below the true melting point. No yield was given, and the substance was said to possess a characteristic sweet odor. This is not shown by the pure substance.

Other investigators have also used the Grignard reaction to prepare mercury dibenzyl, but the yields either have not been given, or have not

[1] Wurtz, *Compt. rend.*, **68**, 1300 (1869); Dreher and Otto, *Ann.*, **154**, 93 (1870). *Cf.* Campisi, *Compt. rend.*, **61**, 861 (1865). The product obtained by the latter melted over 90° higher than pure $(C_6H_5CH_2)_2Hg$.

[2] Pope and Gibson, *J. Chem. Soc.*, **101**, 735 (1912).

exceeded 10%.[3] L. W. Jones reported a yield of 40 g. of mercury dibenzyl by the action of 35 g. of benzylmercuric chloride on benzylmagnesium chloride, but this is obviously an error because the theoretical yield is only 38 g.[4] Apparently the Grignard reaction does not go to completion because it is reported that by means of fractional crystallization it is impossible to separate the mixture of mercury dibenzyl and benzylmercuric chloride formed as a reaction product.[3b] However, treatment of the mixture with copper is said to produce a 75% yield of mercury dibenzyl.[3c] This method has a disadvantage in that it is necessary to carry on the reaction with copper in an inert atmosphere of either nitrogen or carbon dioxide.

A convenient reaction that has been used by the author to prepare mercury diphenyl in excellent yield from phenylmercuric iodide,[5] has been applied successfully to the preparation of mercury dibenzyl. Sodium stannite is one of many reagents used to transform organic mercury compounds of the type RHgX to those of the type R_2Hg.[6] The reaction of the reagent with benzylmercuric iodide is

$$2C_6H_5CH_2HgI + Na_2SnO_2 + H_2O \longrightarrow (C_6H_5CH_2)_2Hg + Hg + 2NaI + Na_2SnO_3$$

Experimental Procedure.—Fifteen grams of benzylmercuric iodide, prepared by the action of mercury on benzyl iodide,[7] was suspended in a solution of 10 ml. of alcohol in 225 ml. of water. A solution containing 25 g. of sodium hydroxide in 125 ml. of water was added to 10 g. of stannous chloride dissolved in 125 ml. of water. This reagent was added to the suspension of benzylmercuric iodide, and the mixture was stirred vigorously with a mechanical stirrer for a period of one hour. At the end of this time the precipitate was filtered off, washed with water, and allowed to dry at room temperature. The mixture was then extracted with acetone. Difficulty was experienced in obtaining a clear filtrate with the extract, so a few grams of powdered zinc was added to amalgamate the finely divided mercury present. After this treatment a clear filtrate was obtained by filtering through an asbestos pad in a Gooch crucible. Water was added to the filtrate until a permanent turbidity was obtained, whereupon cooling to −15° caused the separation of long, needle-like, colorless crystals of mercury dibenzyl, m. p. 111°. The total yield was 64 g. or 93.2% of the theoretical yield.

It has been noted previously in this article[3b,c] that the reaction between

[3] (a) Wolff, *Ber.*, **46**, 64 (1913); (b) Banús, *Anales soc. españ. fís. quím.*, **20**, 667 (1922); (c) Hein and Wagler, *Ber.*, **58B**, 1499 (1925).

[4] Jones, THIS JOURNAL, **40**, 1257 (1918).

[5] Maynard, *ibid.*, **46**, 1510 (1924).

[6] Whitmore, "Organic Compounds of Mercury," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1921, p. 40.

[7] Maynard, THIS JOURNAL, **54**, 2108 (1932).

benzylmagnesium chloride and mercuric chloride leads to a mixture of mercury dibenzyl and benzylmercuric chloride. Since sodium stannite will convert benzylmercuric chloride to mercury dibenzyl, it is suggested that the product of the Grignard reaction be treated with sodium stannite. This procedure would not only eliminate the difficulty of separating the two mercury compounds, but would increase the yield of the desired mercury dibenzyl.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY OF THE
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED FEBRUARY 12, 1932
PUBLISHED MAY 7, 1932

COMMUNICATIONS TO THE EDITOR

THE RELATION BETWEEN THE ACTIVITY OF THE WATER AND THE POTENTIALS OF THE GLASS ELECTRODE

Sir:

In the differential thermodynamic equation recently used to explain the potentials of the glass electrode [M. Dole, THIS JOURNAL, **53**, 4260 (1931)] the correction for possible transference of solvent [see P. B. Taylor, *J. Phys. Chem.*, **31**, 1480 (1927)] was purposely omitted for two reasons. In the first place it was not certain that water could be carried through the glass by ions on the passage of an electrical current, and in the second place the activity of the water was maintained in the actual experiments nearly the same and constant on both sides of the glass membrane; hence if there had been any transfer of water, there would have been no increase or decrease in the free energy of the water as it passed through the glass from one solution to the other and consequently no contribution to the total e. m. f. due to this effect. MacInnes and Belcher [THIS JOURNAL, **53**, 3315 (1931)] have shown that water may be drawn out of the glass, and there have also been recently published [G. Buchböck, *Z. physik. Chem.*, Abt. A, **156**, 232–236 (1931); D. A. MacInnes and D. Belcher, THIS JOURNAL, **53**, 3315 (1931)] data of experiments performed under conditions in which the activity of the water was not maintained constant, but was reduced by the addition of concentrated acids. The observed potentials did not agree with those of the hydrogen–platinum electrode, the resulting error being negative in sign in contrast to the errors of the glass electrode in alkaline solutions which are positive in sign [Dole, *loc. cit.*]. Considering a possible transfer of water, the equation for the glass electrode in acid solutions (where only hydrogen ions are assumed to carry the current across the boundary) becomes

$$E_1 = \frac{RT}{F} \ln \frac{a'_H}{a''_H} + S \frac{RT}{F} \ln \frac{a'_{H_2O}}{a''_{H_2O}} \qquad (1)$$

In this equation a_H is the hydrogen ion activity, S is the number of moles of water carried across the boundary by one mole of hydrogen ions and a_{H_2O} is the activity of the water. If the glass electrode acted as a perfect hydrogen electrode, the equation would be

$$E_2 = \frac{RT}{F} \ln \frac{a'_H}{a''_H} \qquad (2)$$

Subtracting E_2 from E_1, an equation for the error of the glass electrode in acid solutions is obtained, namely

$$\Delta E = E_1 - E_2 = S \frac{RT}{F} \ln \frac{a'_{H_2O}}{a''_{H_2O}} \qquad (3)$$

If the activity of the water is decreased in solution ($'$), the error will be negative, as is actually observed (Ref. 4). In order to test equation (3) further experiments have been carried out in alcoholic solutions and in acid solutions of various salts; they will be fully described in a paper to be submitted shortly for publication. At this time it should be emphasized that this apparent connection between the activity of the water and the proper functioning of the glass electrode must be considered by those who are using or hope to use the glass electrode for determining the P_H in non-aqueous solutions.

MALCOLM DOLE

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED FEBRUARY 16, 1932
PUBLISHED MAY 7, 1932

THE CATALYTIC INFLUENCE OF DRIED CELLULOSE ON THE HYDROLYSIS OF SUCROSE

Sir:

The writers have found that the rate of hydrolysis of sucrose in aqueous solution is subject to a many-fold increase in the presence of dried cellulose fiber at elevated temperatures.

The cellulose fiber which was used as a catalyst in these studies was prepared from the purest quantitative filter paper (Whatman number 43). The paper was disintegrated to a pulp by boiling with distilled water. This treatment was repeated five times with fresh supplies of water. The pulp was pressed into a cake on a Büchner funnel and dried in air at atmospheric pressure at 130–135° for eighteen hours. The fiber was pulled apart with tweezers into a fluffy mass. It was reheated at the same temperature for several hours, and placed in a desiccator over a fresh charge of Dehydrite. Ash determinations on this fiber showed no more than 0.10% of non-volatile matter.

The hydrolysis of the sucrose was brought about by heating a 10% solution of the sugar at 80–85° in a thermostat for several hours. The increase in the rate of hydrolysis of the sucrose was studied originally by the quantitative determination of the ratio between the amount of reducing sugar formed in the control solution (containing no cellulose) and the amount formed in the solution containing cellulose. In later experiments the effect was studied by comparison of the specific rotation of the unhydrolyzed (unheated) sugar solution with that of the control solution, and that of the solution containing cellulose, respectively.

In a typical determination of the relative amounts of reducing sugar formed in the catalyzed and uncatalyzed hydrolysis of sucrose, the controls showed less than 0.01% of reducing sugar, whereas the cellulose catalyzed solutions showed 0.1 ± 0.02% of reducing sugar. This corresponds to a ten-fold difference. A one hundred and thirty-fold difference was observed in an hydrolysis carried out at 96–98°.

The writers are at present investigating the catalytic properties of dried cellulose fiber for the purpose of determining: (1) the conditions best suited to the activation of cellulose fiber; (2) the relationship (if any) between the structure of disaccharides and the effectiveness of dried cellulose fiber in promoting their hydrolysis; (3) the nature of the effect herein described.

A full account of this investigation will be submitted shortly to THIS JOURNAL.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEBRASKA
LINCOLN, NEBRASKA

MARY L. MORSE
W. E. CRAIG

RECEIVED MARCH 10, 1932
PUBLISHED MAY 7, 1932

THEBAINONE

Sir:

The investigations of Clemens Schöpf have shown that the ketone originally called thebainone, resulting from reduction of thebaine with stannous chloride in concentrated hydrochloric acid, contains a new structural skeleton, differing from that present in the starting material. The ketone has been renamed metathebainone. In a recent publication [Schöpf and Hirsch, *Ann.*, **489**, 224 (1931)] the isolation of the true thebainone from the mother liquors of metathebainone preparation is described. In a footnote the statement is made that the true thebainone is undoubtedly different from the "sulfur-free ketone" obtained by Pschorr in 1910 by hydrolysis of β-ethylthiocodide.

In the course of studies which we have been conducting in the thiocodide series we have prepared a quantity of the "sulfur-free ketone" and find it to

be identical in every respect with Schöpf's true thebainone. A sample of the latter, generously supplied by Professor Schöpf, showed no depression in melting point with the "sulfur-free ketone." Schöpf's base shows $[\alpha]_D^{26}$ −45.7°, while Pschorr's shows $[\alpha]_D^{28}$ −46.4°, −46.9° in 95% alcohol. Schöpf bases his statement that the two ketones are different upon discrepancies in the melting points of the methiodide and hydriodide, and the fact that Pschorr's hydriodide is hydrated. The methiodide which we obtain from Schöpf's thebainone sample melts at 250–251°. that from the "sulfur-free ketone" at 251°. When the hydriodide of Schöpf's thebainone is crystallized from a large amount of water, it separates hydrated, and shows two melting points, 163–165° and 257–260°, like the "sulfur-free ketone" hydriodide, whose melting point it does not depress.

The structure of Pschorr's "sulfur-free ketone" is thus settled, and another case of supposed isomerism in the thebainone series eliminated. The true thebainone is obtained in nearly quantitative yield by the hydrolysis of β-ethylthiocodide, which constitutes a very convenient preparative method.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
UNIVERSITY, VIRGINIA
LYNDON F. SMALL
DAVID E. MORRIS
RECEIVED MARCH 17, 1932
PUBLISHED MAY 7, 1932

THE HEAT OF DISSOCIATION OF THE SODIUM MOLECULE

Sir:

The original determination of the heat of dissociation of Na_2 from the band spectrum indicated a value of about 1 volt (= 23,000 cal.). If this were the case saturated sodium vapor should show an abnormal density at all pressures. Rodebush and Walters [THIS JOURNAL, **52**, 2654 (1930)] found this to be true but the abnormality is small and the value of the heat of dissociation calculated from their best results is 0.79 volt (= 18,200 cal.).

Lewis [*Z. Physik*, **69**, 786 (1931)] calculated the heat of dissociation from a vapor density determination by a molecular ray method and obtained the value 0.73 volt (= 16,900 cal.). Recently Nusbaum and Loomis [*Phys. Rev.*, **39**, 179 (1932)] have carried out an accurate analysis of the vibrational bands and find the heat of dissociation to be 0.76 volt (= 17,500 cal.) with an uncertainty of 0.02 volt. It seems quite certain that 0.76 volt is the lower limit and that the true value is in the interval of 0.76–0.78 volt.

CHEMISTRY DEPARTMENT
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
W. H. RODEBUSH
RECEIVED MARCH 28, 1932
PUBLISHED MAY 7, 1932

FERRYL ION, A COMPOUND OF TETRAVALENT IRON

Sir:

Several independent kinetic investigations in this Laboratory have furnished evidence that a compound of tetravalent iron, FeO^{++}, is formed as an intermediate. The results are in agreement with the theory that

$$2Fe^{+++} + H_2O = Fe^{++} + FeO^{++} + 2H^+$$

is a reversible and fairly rapid reaction. The equilibrium constant has the form $K = (Fe^{++})(FeO^{++})(H^+)^2/(Fe^{+++})^2$.

If H_2O_2 reacts with both Fe^{++} and "ferryl ion" but not directly with Fe^{+++}

$$Fe^{++} + H_2O_2 \longrightarrow FeO^{++} + H_2O, \quad -d(Fe^{++})/dt = k_1(H_2O_2)(Fe^{++})$$
$$FeO^{++} + H_2O_2 \longrightarrow Fe^{++} + H_2O + O_2, \quad d(Fe^{++})/dt = k_2(H_2O_2)(FeO^{++})$$

then a steady state will be reached in which $(FeO^{++})/(Fe^{++}) = k_1/k_2 =$ a constant, and the above equilibrium is maintained. The rate of catalytic decomposition of H_2O_2, $-d(H_2O_2)/dt$, is then equal to

$$2k_1(Fe^{++})(H_2O_2) = 2(\sqrt{Kk_1k_2})(H_2O_2)(Fe^{+++})/(H^+) = k(H_2O_2)(Fe^{+++})/(H^+)$$

This rate law was determined by von Bertalan in 1920 and has been confirmed in this Laboratory [Bray, *Chem. Rev.*, **10**, 171 (1932), $k = 0.125$ (not 125) at 40°]. The proposed mechanism explains also the decomposition of H_2O_2 during the very rapid oxidation of Fe^{++} to Fe^{+++}.

If in the reduction of Fe^{+++} by a stannous salt Sn^{++} reacts with FeO^{++} but not with Fe^{+++}, and the equilibrium between 2, 3 and 4-valent iron is established relatively rapidly, the rate law will be $-d(Sn^{++})/dt = k'(Sn^{++})(Fe^{+++})^2/(Fe^{++})(H^+)^2$. This has now been established as a limiting law in solutions in which the only negative ion is ClO_4^-. Also, by raising the temperature and lowering the concentration of Fe^{++}, another limiting condition has been found where the rate is independent of the concentration of Sn^{++}, and the indicated rate-determining reaction is $2Fe(OH)^{++} \longrightarrow Fe^{++} + FeO^{++} + H_2O$.

Other investigators have already observed and studied the retarding effect of ferrous salts during the reduction of ferric salts by hydroxylamine and by iodide. The results of Mitchell [*J. Chem. Soc.*, 336 (1926)] with hydroxylamine and Fe^{+++}, published in 1926, are in accord with the ferryl ion mechanism. In the case of the reactions of iodide with ferric salt and with ferricyanide, Wagner [*Z. physik. Chem.*, **113**, 271 (1924)] in 1924 postulated the formation of I_2^- as an intermediate. There seems, however, to be no supporting evidence for the existence of this compound.

In order to obtain more information about the reaction between Fe^{++} and I^-, Bray and Hershey are studying the reverse reaction between Fe^{++} and I_2. The first experiments, in the presence of AgI, AgBr and Br^-, *i. e.*, at very low concentrations of I^-, are in agreement with the rate law, $-d(I_2)/dt = k''(Fe^{++})(I_2)/(I^-)(H^+)$. This result and the analogy with

other reactions of iodine in aqueous solution have led to the conclusion that the rate-determining reaction is $Fe^{++} + HIO \longrightarrow FeO^{++} + H^+ + I^-$.

Additional experiments have been planned which, it is hoped, will furnish further information about the properties of ferryl ion.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
WILLIAM C. BRAY
M. H. GORIN

RECEIVED MARCH 28, 1932
PUBLISHED MAY 7, 1932

THE EXISTENCE OF NEUTRONS IN THE ATOMIC NUCLEUS

Sir:

In my article on the Arrangement of Protons and Electrons in the Atomic Nucleus [THIS JOURNAL, **53**, 981 (1931)] the discussion was limited to nuclei in which the numbers of protons and electrons are multiples of four and two, respectively. These atoms are by far the most abundant and in terms of the proposed coupling pattern represent the highest symmetry attainable. Although it is not yet possible to make a definite extension to the other nuclear series, it is of interest to discuss the problem briefly in reference to recent investigations.

It appears significant that the next most abundant nuclear type is that which resembles the symmetrical or $4n$ proton type most closely and may be derived from it by the removal of a single proton. This series, *i. e.*, with $4n-1$ protons, follows very closely the $4n$ series: the first and second "extra electron pair" enter at the corresponding atomic numbers. All other nuclei, *i. e.*, those with $4n-2$ and $4n-3$ protons and those with uneven numbers of electrons constitute but a fraction of one per cent. of the atoms of the earth's crust and appear in general to owe their instability to the presence of incomplete or unsaturated groups. More information about nuclear spins and a knowledge of the coupling rules in these cases are necessary before definite conclusions can be drawn regarding these structures. At present we can only discuss certain possibilities.

As an illustration we may consider carbon 13. In the accompanying figure, this nucleus is pictured in the same symbols formerly employed, a proton, or the direction of the proton spin vector, by a bar and an electron pair by a ball. The structure is the same as that of carbon 12 plus one proton and one electron (half ball). Of course we do not know where the extra proton is coupled but we do know that such a bond of two protons and one electron as suggested in the figure (two bars and the half ball) is stable from the existence of the hydrogen isotope [Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 154 (1932)] of mass 2. Beryllium 9 must also contain such a group and when it captures a high speed alpha particle to form carbon 13 it is not difficult to imagine that occasionally the loosely bound

proton and electron are detached and emitted as a neutron leaving carbon 12, as postulated by Chadwick [*Nature*, **129**, 312 (1932)].

The essential point may be stated in this way. In the proposed structure alpha particles and neutrons do not exist as such in any nucleus, merely protons and electrons coupled in a certain definite pattern. When these couplings are broken, alpha particles and electrons in pairs are normally formed as in the radioactive series. However, it should also be possible to break the bonds in such a way as to give neutrons, mass one or two, hydrogen, mass one or two, helium mass 5, etc., and it is to be expected that such particles would be formed more readily from nuclei containing unsymmetrical or unsaturated groups.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

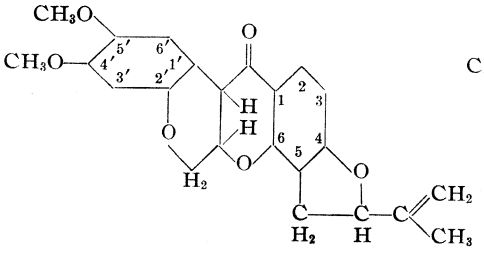
WENDELL M. LATIMER

RECEIVED APRIL 4, 1932
PUBLISHED MAY 7, 1932

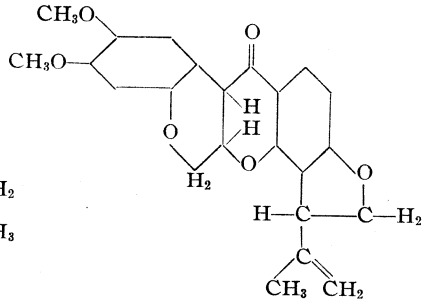
ROTENONE. XXI. THE STRUCTURE OF ISOROTENONE, β-DIHYDROROTENONE AND DEHYDROROTENOL

Sir:

In a recent publication [S. Takei, S. Miyajima and M. Ōno, *Bul. Inst. Phys. and Chem. Research* (Tokyo), **11**, 1–4, Feb. 1932] Takei and his associates proposed a formula for rotenone which differs from the one (I) proposed by us [F. B. LaForge and H. L. Haller, THIS JOURNAL, **54**, 810 (1932)] only in the point of attachment of the isopropenyl side chain on the substituted dihydrocoumarone ring as indicated in formula II.



I



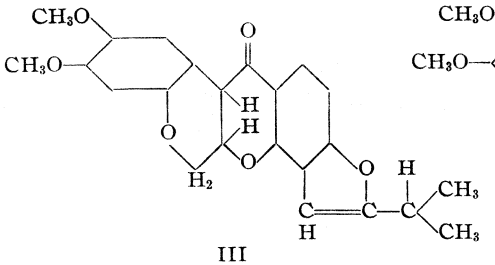
II

The formula of Takei takes no account of the loss of optical activity by cleavage of the oxygen bridge with the resultant formation of the phenolic hydroxyl in position 4 by hydrogenation of tubaic acid and the analogous formation of tetrahydro derivatives from other rotenone derivatives. Moreover, the mechanism suggested by us is strongly supported by analogy with that of certain codeine derivatives, which is referred to in a previous article [H. L. Haller and F. B. LaForge, THIS JOURNAL, **54**, 1988 (1932)].

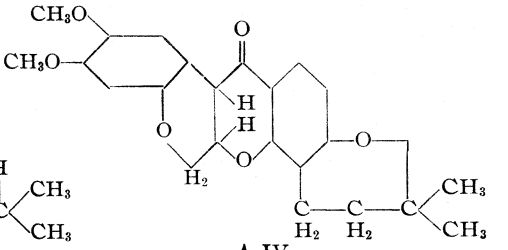
Both these results are to be expected from the groupings present in formula I but would not be possible according to Takei's formula II.

As the complete formula for rotenone is now known, it is possible to propose a formula for isorotenone [S. Takei, *Biochem. Z.*, **157**, 1 (1925); *Ber.*, **61**, 1003 (1928)] and for β-dihydrorotenone. [H. L. Haller, THIS JOURNAL, **53**, 733 (1931)]. However, a modification of the structure proposed for dehydrorotenol [H. L. Haller and F. B. LaForge, THIS JOURNAL, **53**, 2271 (1931); F. B. LaForge, H. L. Haller, and L. E. Smith, THIS JOURNAL, **53**, 4403 (1931)] is necessary.

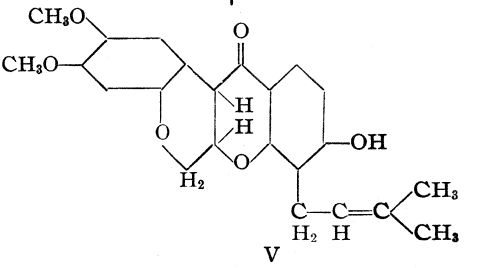
It has been shown that rotenone and isorotenone differ from each other in the position of a double bond. Therefore, structure III, which accounts for all the facts, is proposed for isorotenone.



III



IV



V

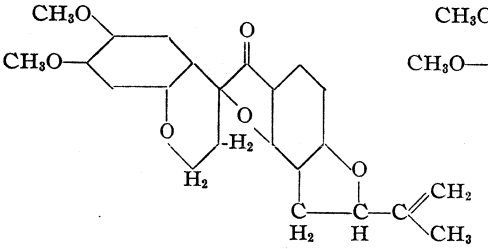
β-Dihydrorotenone (IV), an isomer of dihydrorotenone, which gives many of the typical reactions of dihydrorotenone, is obtained when rotenonic acid (V) is dissolved in a solution of acetic and sulfuric acids. The formation of β-dihydrorotenone is in a measure analogous to the formation of a saturated lactone by the isomerization of an unsaturated acid.

Dehydrorotenol, which is obtained on mild oxidation of rotenol, is colorless, unlike all other dehydro derivatives of the rotenone series, which are yellow. It also differs from these in that it can be reconverted into rotenol by reduction.

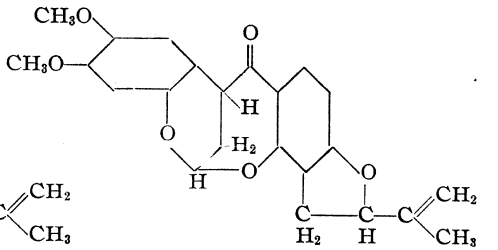
Dehydrorotenol, like rotenol, can be hydrogenated to a tetrahydro derivative which is alkali soluble but which differs from the tetrahydrorotenol (dihydrorotenolic acid) in that it is not cleaved by alkaline hydrogen peroxide. Rotenol possesses a free hydroxyl group in the tubaic acid half of the

molecule, and this free hydroxyl group is essential for the cleavage of the carbonyl group with alkaline hydrogen peroxide. It follows therefore that this group is not present in dehydrorotenol. Rotenol gives a color test with ferric chloride, whereas dehydrorotenol does not. Thus it follows that the hydrogen atom of the free hydroxyl group is involved in the formation of dehydrorotenol. If the original ether linkage in rotenone was reformed in the formation of dehydrorotenol from rotenol, dehydrodihydrorotenolic acid and *dl*-dihydrorotenonic acid [H. L. Haller and F. B. LaForge, THIS JOURNAL, **53,** 3426 (1931)] should be identical as the asymmetric center I [*ibid.*, p. 3427] is racemized in the formation of rotenol. Besides, dehydrorotenol does not react with iodine and alcoholic potassium acetate to lose two hydrogen atoms and to form dehydrodihydrorotenone. It is possible, therefore, that the structure for dehydrorotenol is either VI or VII.

The product obtained from dehydrodihydrorotenolic acid and acetic anhydride, which was thought to be a mixed anhydride [H. L. Haller and F. B. LaForge, THIS JOURNAL, **53,** 2271 (1931)], is in fact a true acetyl derivative, the hydroxyl group in the 4 position having been acetylated.



VI



VII

INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.

RECEIVED APRIL 4, 1932
PUBLISHED MAY 7, 1932

H. L. HALLER

THE RELATION BETWEEN THE DISSOLUTION OF METALS IN ACIDS AND THE ELECTROLYTIC EVOLUTION OF HYDROGEN

Sir:

The finding of Brönsted and Kane [THIS JOURNAL, **53,** 3624 (1931)] that the velocity of the reaction of sodium amalgam with aqueous solutions is proportional to a fractional power of the concentration of sodium in the amalgam suggests strongly that the rate of hydrogen evolution on a sodium amalgam surface is essentially the same as on a mercury surface polarized electrically to a potential equal to that established by the sodium–sodium ion equilibrium. From the precise and definitive work of Bowden [*Trans.*

Faraday Soc., **24,** 473 (1928)] we know that the coefficient n in the Tafel polarization equation

$$E = \frac{RT}{nF} \ln I + \text{constant}$$

is 0.5 on mercury surfaces at current densities below about 10^{-4} amp. per sq. cm., and changes discontinuously at higher current densities to 0.27. Since

$$E = \frac{RT}{F} \ln \frac{a_{Na^+}}{a_{Na}} + E_0$$

and since current is proportional to reaction velocity, the above hypothesis indicates such a fractional order of reaction as was found.

$$v \propto \frac{[Na]^n}{[Na^+]^n}$$

This assumes, of course, that these amalgams are so dilute that there is approximate proportionality between activity and concentration of the sodium.

It also follows that the reaction velocity should vary inversely as the same fractional power of the sodium-ion activity. While Brönsted and Kane seem not to have expected any such effect, and report no quantitative results on the effect of sodium ion, they do report that addition of sodium chloride decreases the reaction velocity.

It should therefore be possible to apply to the amalgam reaction all of the electrochemical evidence that the reaction $H^+ + e \rightleftharpoons H$ is reversible and very rapid compared with the process of formation of H_2 from the atomic hydrogen or its alloy with the metal. In particular it is extremely difficult to understand the saturation effects observed in the electrochemical oxidation of hydrogen to hydrogen ion [see Hammett, THIS JOURNAL, **46,** 7 (1924)] on the basis of any other mechanism.

The contrary conclusion of Brönsted and Kane that the first step in the formation of molecular hydrogen from hydrogen ion is the rate-determining one depends upon their observation of a direct effect of the concentration of the reacting acid upon the velocity. This would be strong evidence if it could be proved that diffusion was not a factor in the determination of the reaction velocity in their experiments and in those of Kilpatrick and Rushton [*J. Phys. Chem.*, **34,** 2180 (1930)]. Certainly Bowden showed that the electrolytic evolution of hydrogen on mercury is determined by hydrogen-ion concentration and is subject to no generalized acid effects when the reaction velocity is so low that diffusion is not a significant factor.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

LOUIS P. HAMMETT
ARTHUR E. LORCH

RECEIVED APRIL 5, 1932
PUBLISHED MAY 7, 1932

THE ELECTROMOTIVE FORCE OF CELLS CONTAINING DILUTE HYDROCHLORIC ACID

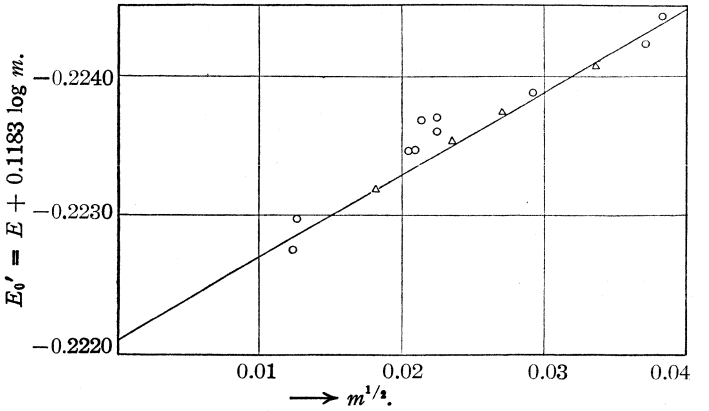
Sir:

In a recent paper Carmody [THIS JOURNAL, **54,** 188 (1932)] has published the results of some very accurate measurements of the e. m. f. of cells containing dilute solutions of hydrochloric acid. Mainly owing to the use of silica vessels these results differ from those of Linhart [THIS JOURNAL, **41,** 1175 (1919)] and of Nonhebel [*Phil. Mag.* [7] **2,** 1085 (1926)] but it can be shown that the results of these earlier workers are not incompatible with those of Carmody.

It has been suggested elsewhere [*J. Phys. Chem.*, **31,** 1647 (1927)] that the conductivity data for strong acids and bases in dilute solution can be corrected for the effect of impurities by the equation

$$\Lambda = \Lambda_0 - bc^{1/2} - k/c$$

where b is a constant calculable from Onsager's theory or determinable experimentally and k is a measure of the amount of acid removed by the



○, Nonhebel; △, Carmody.

Fig. 1.

impurities which either have dissolved from the glass or were originally present in the water. By the courtesy of Sir Harold Hartley, F.R.S., I have been able to avail myself of some measurements by Marshall on the conductivity of dilute solutions of hydrochloric acid in cells of similar glass and water of comparable conductivity to those employed by Nonhebel. Using the above equation, I have calculated from these data that Nonhebel's results are about 0.0010 volt high at 0.0001 molal and 0.0001 volt high at 0.001 molal. Even Carmody's results require a slight correction which can be calculated from the recent conductivity data of Jeffery and Vogel [*J. Chem. Soc.*, 400 (1932)], who employed silica cells and water of

about the same conductivity as that used by Carmody: the correction lowers Carmody's most dilute point by 0.00012 volt.

The corrected data are plotted in the accompanying diagram and the straight line is drawn with the slope required by the limiting equation of Debye and Hückel. It is evident that the agreement is satisfactory and that the most probable value of E_0 is 0.2221 volt, which is the value previously adopted by Randall and Young [THIS JOURNAL, **50**, 989 (1928)].

THE UNIVERSITY
READING, ENGLAND
W. F. KENRICK WYNNE-JONES

RECEIVED APRIL 13, 1932
PUBLISHED MAY 7, 1932

THE ESTIMATION OF IRON IN SOLUTIONS CONTAINING BOTH BIVALENT IRON AND TRIVALENT TITANIUM

Sir:

It is known that sulfuric acid solutions of ferrous sulfate undergo oxidation but very slowly at room temperatures.[1] Thus, Baskerville and Stevenson[2] found that upon passing air for twelve hours through a sulfuric acid solution of Mohr's salt, there resulted but 0.0001 g. of Fe^{+++} out of a total of approximately 0.71 g. of Fe^{++}.

Furthermore, titanous sulfate solutions of ordinary acidity are extremely unstable in air. Thus, while reduction of titanium in the Jones reductor proceeds quantitatively to the trivalent condition, the deoxidized substance is usually collected under a protective solution, such as ferric sulfate, whereby the titanium is immediately converted to the quadrivalent state with the formation of an equivalent amount of the more stable ferrous sulfate.[3]

These facts, namely, the stability of acidified ferrous sulfate solutions and the instability of acidified titanous sulfate solutions toward atmospheric oxidation, suggested the possibility of estimating Fe^{++} in the presence of Ti^{+++} by subjecting the solution containing these ions to an air-bubbling process. It was hoped that in the time required to effect the complete oxidation of the Ti^{+++} the amount of Fe^{++} oxidized would be negligible, so that titration of the aerated solution with standard potassium permanganate would give a value corresponding to the iron alone.

This hope has indeed been realized and we have found that results obtained by the method outlined above are in good agreement with those obtained by the well-known method of Gooch and Newton,[4] wherein the Ti^{+++} is oxidized by bismuth trioxide, which does not affect the Fe^{++}, the metallic bismuth thus precipitated and excess bismuth oxide removed by

[1] McBain, *J. Phys. Chem.*, **5**, 623 (1901).

[2] Baskerville and Stevenson, THIS JOURNAL, **33**, 1104 (1911).

[3] Lundell and Knowles, *ibid.*, **45**, 2620 (1923); *Ind. Eng. Chem.*, **16**, 723 (1924).

[4] Gooch and Newton, *Am. J. Sci.*, **23**, 365 (1907); Newton, *ibid.*, **25**, 343 (1908).

filtration, and the filtrate, containing the Fe^{++}, titrated with standard permanganate in the usual manner.

Lundell and Knowles[5] have shown that sulfuric acid solutions of uranous sulfate, like ferrous sulfate, exhibit marked stability toward air oxidation, and we hope to employ our differential oxidation procedure in the evaluation of uranium in solutions containing U^{++++} and Ti^{+++}.[6] Other determinations, involving similar combinations, suggest themselves as possibilities in the further application of this method.

In the course of this work, a technique has been developed for the preparation of very pure solutions of titanic sulfate and titanous sulfate.

We expect to publish a complete account of this work in the near future.

[5] Lundell and Knowles, THIS JOURNAL, **47**, 2637 (1925).

[6] *Cf.* Newton and Hughes, *ibid.*, **37**, 1711 (1915).

[7] J. T. Baker Chemical Company Fellow in Analytical Chemistry, 1930–1931.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

WILLIAM M. THORNTON, JR.
REUBEN ROSEMAN[7]
SAMUEL I. KATZOFF

RECEIVED APRIL 20, 1932
PUBLISHED MAY 7, 1932

PENTAVALENT BORON

Sir:

A compound of boron has been prepared which has the formula BR_3Na_2 in which R is the α-naphthyl group. This compound seems to be of a type not heretofore known and to be of particular interest from the standpoint of valence theory.

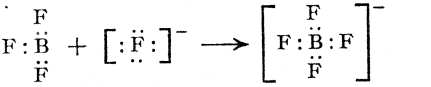
The compound has been prepared by treating tri-α-naphthyl boron in ether solution with 40% sodium amalgam in the absence of air and water.[1] The solution turns first yellow and finally black as the reaction progresses. Upon hydrolyzing the ether solution and titrating with acid the number of mols of sodium was found to be twice (1.97–1.98) the number of mols of the tri-α-naphthylboron originally introduced into the solution. The compound was then prepared in crystalline form from a mixture of ethyl ether and petroleum ether. It is nearly black in color, somewhat resembling iodine in appearance. This material was analyzed for sodium and boron. A second crop of crystals was obtained from the mother liquor. This had the same appearance and gave the same analysis. The analyses indicated one molecule of ether of crystallization, which was removed quantitatively by evacuating and heating to 175°. The first analysis given below is for the first crop of crystals, the second for the crop

[1] A solution of this compound was undoubtedly first obtained by Krause and Nobbe [*Ber.*, **63**, 934 (1930)] but inasmuch as they did not analyze their product they naturally assumed that it was a monosodium addition compound as in the case of triphenylboron.

from the mother liquor before heating and the third for this same material after heating to remove ether.

Anal. Calcd. for $C_{30}H_{21}BNa_2$: Na, 10.50; B, 2.47. Found: Na, 10.59; B, 2.49. Calcd. for $C_{34}H_{31}OBNa_2$: Na, 8.98; B, 2.11. Found: Na, 8.92; B, 2.15. Calcd. for $C_{30}H_{21}BNa_2$: Na, 10.50; B, 2.47. Found: Na, 10.53; B, 2.40.

Compounds of boron showing a valence of more than three are of course known, such as KBF_4. In such cases an octet is completed by four covalent bonds thus



No compound has been reported, however, in which the boron completes its octet by taking two electrons from different atoms to give ionic linkages. Thus no compound is known of the formula Na_2BF_3. It now appears that in case the three fluorine atoms are replaced by three naphthyl groups, then the boron atom can complete its octet by taking two electrons from two sodium atoms. How these sodium atoms are held is a question to be decided by further experiment. This work is being continued.

DIVISION OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

HENRY E. BENT
MAURICE DORFMAN

RECEIVED APRIL 23, 1932
PUBLISHED MAY 7, 1932

THE ACTIVATOR OF CATALASE[1]

Sir:

The activation of glandular proteinase (cathepsin) by glutathione[2] and other —SH compounds points to a connection between enzymic hydrolysis and the sulfur oxidation–reduction system of Hopkins. A connection of the sulfur system to enzymic oxidation is also indicated, however, by our findings that the catalase activity (of pig's or lamb's liver) is increased by S–S derivatives, namely, cystine, insulin and oxidized glutathione. In liver juice, which contains sulfhydryl derivatives, the catalase may therefore be activated by all manner of oxidizing agents, such as iodine, ferric iron, oxygen and hydrogen peroxide, so that in the usual preparations of catalase the enzyme will be found completely active.

The natural activator which occurs in the liver press juice is not cystine, since in larger amounts this again inhibits the catalase action, but in view of the quantity of glutathione present in liver, it may be that the natural activator is, in part at least, composed of oxidized glutathione.

Since the presence of –SH derivatives accelerates proteolysis, and that of S–S derivatives, the decomposition of hydrogen peroxide, it would there-

[1] Food Research Division Contribution No. 145.

[2] *Naturwissenschaften*, **18**, 645 (1930).

fore seem that the state of the S–S – SH equilibrium determines whether the cell at the moment functions proteolytically or oxidatively.

BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.

A. K. BALLS
W. S. HALE

RECEIVED APRIL 26, 1932
PUBLISHED MAY 7, 1932

NEW BOOKS

Matière et Atomes. (Matter and Atoms.) By A. BERTHOUD, Professor of Physical Chemistry at the University of Neuchâtel. Second edition. G. Doin et Cie, 8 Place de l'Odéon, Paris, France, 1932. 324 pp. 28 figs. 11.5 × 18 cm. Price, 26 fr.

This is a revised and enlarged second edition of "New Conceptions of Matter and the Atom." The earlier book has been conscientiously revised and brought up to date. The present chapters include: Historical Introduction, Classical Theories of Light and of Electrons, Theory of Relativity and Mass, x-Rays and Atomic Numbers, Radioactivity and Isotopes, Rutherford Atom and Transmutation, Bohr Atom and Quantum Theory, Complex Atoms, x-Rays and Chemical Affinity, Wave Mechanics.

The style is clear and readable throughout and the selection of material judicious. The book is addressed to "a wide circle of cultivated readers," and the plan is to present selected facts, intelligently grouped, and then to state the conclusions drawn from them. The names of Prout and Proust are frequently confused.

NORRIS F. HALL

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. System-Number 7. **Bromine.** Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. xxi + 342 pp. 17 × 25 cm. Price, to subscribers, M. 56; singly, M. 49.

This volume presents the chemistry of bromine itself and of its compounds with those elements of smaller System-Numbers (1–6): namely, chlorine, fluorine, nitrogen, oxygen, hydrogen and the inert gases. The relevant literature has been covered up to August 1, 1931.

The great extension of our knowledge of this element, since the previous edition, particularly as regards its physico-chemical properties and those of its compounds, is most impressive. Attention should also be called to the section on the history of our knowledge of this element and on its economics.

The present volume is a worthy addition to this invaluable encyclopedia of inorganic chemistry.

ARTHUR B. LAMB

The Corrosion of Metals. Part II. **Special Researches Concerning the Dissolving of Metals.** By Professor WILH. PALMAER, D.Sc. Proceedings of the Royal Swedish Institute for Engineering Research 100,108. Svenska Bokhandelscentralen A.-B., Stockholm, Sweden, 1931. 198 pp. 51 figs. 10 plates. 16.5 × 24 cm.

Part I of this Memoir (in English) dealing with the General Theory of Corrosion has already been reviewed in THIS JOURNAL [Vol. **51**, p. 3172 (1929)].

In the present Part II (also in English) a further series of experimental investigations are reported which confirm the conclusions reached in Part I, namely, that the primary factor in the corrosion of metals is the activity of local galvanic elements. The specific materials studied here are malleable cast iron, soft iron, electrolytic iron and certain other pure metals and amalgams. Special chapters are devoted to the alleged formation of a hydrogen film on dissolving metals, the theory of resistance capacity, the theory of isohydric solutions, the occurrence of an induction period, the diffusion theory of corrosion and a criticism of the work in this field of Centnerszwer and his collaborators.

Part III, which is to deal with the special theory of the corrosion of iron, is being prepared for the press.

ARTHUR B. LAMB

Chemisches Fachwörterbuch. Für Wissenschaft, Technik, Industrie und Handel. (Chemical Dictionary for Science, Industry and Business.) Edited by A. W. MAYER. Vol. II. English-German-French. Verlag von Otto Spamer, Heinrichstrasse 9, Leipzig C 1, Germany, 1931. 943 pp. 18 × 25.5 cm. Price, Rmk. 70; bound, Rmk. 75.

Volume I (German-English-French) of this three-volume work was reviewed by the present reviewer on page 1614, Volume **53**, 1931, THIS JOURNAL. Volume II (English-German-French) is fully as complete and more voluminous than the first volume, containing 943 pages, and is unquestionably well done. Little can be said that was not said about the first volume, for one will find here undoubtedly the best scientific chemical dictionary available. It should enable not only the scientific man but the industrial and technical expert to find quickly the equivalent German and French word or phrase for almost any like phrase in English, with various synonyms as well. It will be invaluable to any translator whether interested in scientific or chemical trade literature. Volume III (French-German-English) will appear later.

The reviewer has the greatest respect and wonder for the persistence, detailed investigation and untiring labor which the author has put into its production. The statement in the first review applies equally to this: *viz.*, those who are fortunate enough to have this volume in their libraries should have no difficulty in obtaining a correct French or German equiva-

lent for almost any English word or technical phrase required in chemical parlance.

CHARLES L. PARSONS

Die Katalyse. Die Rolle der Katalyse in der analytischen Chemie. (Catalysis. The Role of Catalysit in Analytical Chemistry.) By Dr. GERTRUD WOKER. II. Special Part, Second Section, Biological Catalysts. Second Half, Atmungsfermente. Verlag von Ferdinand Enke, Stuttgart, Germany, 1931. xix + 592 pp. 2 figs. 16.5 × 25.5 cm. Price, unbound, RM. 76; bound, RM. 79.

This is hardly a treatise on analytical chemistry, it is really a monograph on a special group of the enzymes, those which are associated with the mechanisms of fermentation and oxidation.

The first two hundred pages are devoted to zymase and the various enzymatic phenomena which are encountered in fermentation problems. In this section there is an extended discussion of the chemical mechanism of fermentation, including the intermediate products, methods whereby intermediate products may be isolated or identified and the inter-molecular and intra-molecular reactions which such products may undergo.

Those who are interested in the chemistry of the physiology of the action of insulin will find in this section an excellent discussion of certain theories of its action. Insulin is regarded as the "coenzyme" of tissue zymase. The mixture; α,β-glucose + H_3PO_4 + the synthesizing enzyme, phosphatese + insulin, results in the formation of γ-glucosediphosphate which breaks down in the organism to yield γ-glucose which, because of its great instability, is readily oxidized. Incidentally the graphic formulas of many of the sugars as given do not conform to our best present knowledge. Thus the normal form of glucose is given as containing the 1,4-oxide ring instead of the correct 1,5-oxide ring and γ-glucose is depicted as possessing the 1,6-oxide ring instead of the 1,4-oxide ring. Accordingly in the section on insulin action, the reader should recognize that while the discussion of the mechanism of the reaction may be correct, the formulas which depict the probable reactions are incorrect.

The second section of 335 pages deals with the oxidases, peroxidases and reductases, and here again all phases of the chemistry of the action of this important group of enzymes are considered in detail. The various theories of oxidation are considered at length and the evidence for or against each theory is excellently presented. The systems considered range in complexity from simple inorganic systems to such complex biological systems as the purines and amino acids. Here the reviewer notes an inexplicable omission. In spite of the fact that the cystine $\rightleftarrows$ cysteine reaction is considered at some length, glutathione is mentioned only once and that only casually in a footnote (p. 196) in the section on fermentation.

The book is not strictly up to date. The reviewer did not make a de-

tailed search to determine the date of the latest reference cited, but a general inspection failed to locate any references to literature later than 1928. As a monograph on this special group of enzymes prior to that date it is highly recommended.

ROSS AIKEN GORTNER

Kapillarchemie. (**Capillary Chemistry.**) A Presentation of the Chemistry of the Colloids and of Related Fields. By Prof. Dr. HERBERT FREUNDLICH, Member of the Kaiser Wilhelm-Institut für Physikalische Chemie und Elektrochemie. Vol. II. Fourth edition. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1932. xi + 955 pp. 113 figs. 17.5 × 25 cm. Price, unbound, M. 60; bound, M. 69.

The first volume of the fourth edition of this handbook, treating the general principles of the subject, appeared in 1930 and has already been reviewed in THIS JOURNAL [**52,** 3033 (1930)]. The present second (and last) volume discusses the properties and behavior of individual, colloidally dispersed systems.

This volume follows closely the order of treatment and subdivisions of the previous edition. The revision has, however, been a thorough one. The many researches that have appeared in the intervening ten years have been thoroughly considered and incorporated. As a consequence many parts have been completely rewritten and many entirely new chapters or subdivisions have been added, such, for instance, as those discussing the anisotropy of colloidal solutions, the hydrosols of the proteins and the behavior of gels. All told, the number of pages in this volume represents an increase of more than fifty per cent. over the number of pages in the corresponding part of the last edition.

This edition, like its predecessors, is not merely a comprehensive survey of an immense field; it is a critical, thoughtful and penetrating discussion of that field, replete with illuminating deductions and suggestions. It constitutes an impressive intellectual achievement.

Needless to say, it remains an invaluable handbook of colloid chemistry and of related branches of our science.

ARTHUR B. LAMB

A Shorter Course in Organic Chemistry. By J. C. COLBERT, Assistant Professor of Chemistry in the State University of Oklahoma. The Century Co., 353 Fourth Avenue, New York, 1931. xviii + 352 pp. 15 × 22 cm. Price, $3.60.

This is a book which both merits and needs another edition. The conversational tone of the book is in refreshing contrast to the proverbial dryness of textbooks; many charts are used to give the student a "birds-eye view" of structural relationships; and in the index when two names refer to the same substance, page numbers are given in both places. The author's judgment as to the division of space between the branches

of organic chemistry is good, and the illustrative material includes such up-to-date references as "Jake" paralysis and the Cleveland Clinic disaster.

On the other hand, the book is marred by a multitude of minor errors, not all of which can be blamed on the compositor. In a book particularly designed for premedical students it is strange to find no mention of carotene, and no reference to Vitamin D. The normal blood sugar content is stated on p. 203 to three significant figures, and the uses of hexylresorcinol as an external antiseptic and an anthelminthic are not only not mentioned, but are by implication disavowed, p. 308. The "hemlock" of Socrates is not the hemlock with which most readers of the book will be familiar.

The configuration of *d*-glucose on p. 199 is the enantiomorph of that on p. 195, and starch is pictured as derived from *d*-allose, p. 212, with the warning that no attention has been given to the position in space of the hydroxyl groups and the lactone rings. The discussion of the polariscope on pp. 160–161 gives the impression that tourmaline rather than calcite is used in Nicol prisms. The discussions of amino acids and of indicators could be improved if the author would recognize "intramolecular ionization," but the references to J. U. Nef on pp. 43, 44, 82, 128 and 285 are not calculated to help the student.

ELLIOT Q. ADAMS

Ergebnisse der Enzymforschung. (Reviews of Enzyme Research.) Edited by F. F. NORD and R. WEIDENHAGEN. Vol. I. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1932. xi + 377 pp. 63 figs. 16 × 24 cm. Price, M. 27; bound, M. 29.

This book contains seventeen chapters on various phases of recent enzyme research. Each chapter is written by a different author and represents a critical rather than comprehensive treatment of a particular problem. Among a number of general problems considered are the thermodynamics of cell reactions; the significance of oxidation–reduction potentials; the physico-chemical mechanism of enzyme action; bacterial enzyme reactions; and the formation of enzymes. The more specific problems treated are alcoholic fermentation; proteolytic enzymes; carbohydrases and their specificity; acetic acid fermentation; tyrosinase; bone phosphatase; crystalline urease; crystalline pepsin; the oxygen-carrying ferment of respiration; and the biochemistry of the lower fungi. Additional volumes will presumably appear covering an expanded range of topics.

A highly commendable feature is that the collaboration is international, involving German, English, American and French workers. Leaders of the respective fields have been secured for the most part. The personal outlook of each collaborator is strongly emphasized, and very often a con-

siderable summary of his own work is reported. Willstätter, Euler, J. B. S. Haldane and Waldschmidt-Leitz do not write chapters in the present volume.

The book is written by the expert for the expert and will consequently be of greatest use to the research worker. It raises problems quite as much as it presents their solutions.

DEAN BURK

Ergot and Ergotism. A Monograph Based on the Dohme Lectures Delivered in Johns Hopkins University, Baltimore. By GEORGE BARGER, F.R.S., Professor of Chemistry in Relation to Medicine in the University of Edinburgh. Gurney and Jackson, 33 Paternoster Row, E.C., London, England, 1931. xvi + 279 pp. 15 × 23 cm. 41 figs. Price, 15 s., net.

In the preface the author remarks that "this book was planned more than twenty years ago during a happy partnership in research" (with H. H. Dale) but that other activities caused its abandonment. It is most fortunate now that the author has returned to this plan by taking the opportunity to expand his recent Dohme Lectures into the present invaluable monograph. There is now placed at our disposal a work in which for the first time the essential facts about ergot and ergotism have been gathered together and critically presented by the outstanding authority on the subject. The book is gracefully dedicated to the memory of Charles Tanret, the discoverer of ergotinine, ergothioneine and a pioneer worker with ergosterine. In spite of the diversity of the topics and the compactness of presentation, it is written in a most interesting, clear, readable and scholarly fashion.

The first chapter deals with the history and distribution of rye and of ergot and the early obstetrical use of ergot which resulted eventually in its introduction into official medicine first in the United States and later in European countries. The second chapter discusses the two types of ergotism—convulsive and gangrenous—from descriptive, historical and geographical standpoints. The interesting suggestion is developed that deficiency in Vitamine A is a probable factor in convulsive ergotism. A third chapter is devoted to the botany of the ergot fungus, its life cycle and its relation to agriculture. There follows a description of the numerous species of *Claviceps* and of the so-called "biological" races characterized by their infectiousness for definite hosts.

This is followed by a chapter on the chemistry of ergot—brought right up to date—containing the essentials of what is known concerning the substances peculiar to it, *viz.*, the alkaloids ergotoxine, ergotinine, ergotamine and ergotaminine, and which are responsible for its characteristic physiological action. Discretion is used in regard to the space devoted to other constituents.

The fifth chapter discusses fully the pharmacology and the toxic effects of the alkaloids and of the other active amines, such as histamine, which are found in ergot. The last chapter is devoted to ergot in the pharmacopoeias and to the methods of making extracts and assays and finally to ergot in forensic medicine.

A most valuable feature is the extensive bibliography which ends the volume and which bears witness to the industry and thoroughness of the author in preparing this work. Because of the complexity of the material presented, the plan of dividing the various chapters into paragraphs with appropriate headings has been found most useful to the reader. These together with the page headings are distinct aids for ready reference. Finally, excellent judgment has been used in the inclusion of the illustrations to be found in the book.

WALTER A. JACOBS

BOOKS RECEIVED

March 15, 1932–April 15, 1932

C. DRUCKER AND E. PROSKAUER. "Physikalisch-chemisches Taschenbuch." Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 546 pp. M. 27.50; bound, M. 29.

WILLIAM T. HALL. "Treadwell-Hall. Analytical Chemistry. Qualitative Analysis." Eighth English Edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 640 pp. $4.50.

ARTHUR HARDEN. "Alcoholic Fermentation." Fourth edition. Longmans, Green and Company, 55 Fifth Ave., New York. 243 pp. $5.50.

JITENDRA NATH RAKSHIT. "Association Theory of Solution and Inadequacy of Dissociation Theory." S. C. Auddy & Co., Booksellers and Publishers, 58 & 12, Wellington St., Calcutta, India. 298 pp.

LEON B. RICHARDSON. "General Chemistry." Revised edition. Henry Holt and Company, One Park Avenue, New York. 779 pp. $3.50.

Recueil des Travaux Chimiques des Pays-Bas. "Tables Générales des Tomes 1–50." Vol. I. Tables des Tomes 1–38. Édition de la Société Chimique Neerlandaise. Imprimerie de la Soc. an. de Erven Loosjes à Haarlem, Holland. 416 pp.

The Journal of the American Chemical Society

VOL. 54 JUNE, 1932 No. 6

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE SPACING OF NON-POLAR MOLECULES IN CRYSTAL LATTICES. THE ATOMIC DOMAIN OF HYDROGEN. A NEW FEATURE OF STRUCTURE OF THE BENZENE RING

BY EDWARD MACK, JR.[1]

RECEIVED SEPTEMBER 25, 1931 PUBLISHED JUNE 6, 1932

Our knowledge of the structure of the crystal lattices of organic compounds is gradually increasing. But the progress is dishearteningly slow, due, of course, to the very great difficulties inherent in the problem. Several score of organic crystals have been subjected to x-ray analysis. In by far the larger number of these cases the analysis has not been rigorous enough to do more than tell us the dimensions of the unit cell and define the space group, if indeed it tells us as much as this. In only a very few cases has the more intimate structure been indicated, the orientation of the molecules with respect to the crystal axes and the arrangement and spacing of the atoms within the molecule.[2] One of the most disappointing features of the present technique of x-ray analysis is its inability to locate the hydrogen atoms. Most organic molecules contain a larger population of hydrogen than of any other kind of atom, and as a rule the hydrogen atoms, because of their single valence bond, occur at the ends or on the exterior surface of the molecule. As a consequence, x-ray analysis of an organic crystal generally presents us with a picture of a three-dimensional array of molecules hung in empty space, with large gaps between neighbor molecules, a picture more like that of a gas than of a solid. A question which immediately comes to mind is whether such intervening spaces can be filled up, by attachment of the missing hydrogen atoms on the proper chemical bonds, so that neighbor molecules then interlock. The present paper undertakes, in part, to answer this question.

In "A Note on the Crystalline Structure of Certain Aromatic Compounds," Sir William Bragg[3] remarks "when cell dimensions and space

[1] Guggenheim Memorial Fellow, 1929.

[2] For an excellent critical review of this field up to about the end of the year 1930, see "Crystal Structures of Organic Compounds" by Sterling B. Hendricks, *Chem. Rev.*, **7**, 431 (1930).

[3] Bragg, *Z. Krist.*, **66**, 24 (1927).

group have been determined the really difficult and the more fascinating problem still remains in finding the distribution of the atoms in space." In the present, although undoubtedly only temporary, default of x-ray intensity methods in determining the lattice positions of atoms in most of these aromatic molecules, the present author wishes to advance a stereochemical solution of some of these three-dimensional picture puzzles. The solution is based on the theory that the benzene ring is the flat graphite ring, a contention strongly supported[4] by the rigorous analysis which Mrs. Lonsdale has made of the structure of crystalline hexamethylbenzene.[5] From a stereochemical consideration of the probable structures of these aromatic crystals, we shall be able to draw some consistent conclusions regarding the size of the hydrogen atom, and shall also be led to the proposal of a new feature of structure for the benzene ring, based, as will be seen, on empirical evidence.

To begin with, before we proceed to a consideration of the size of the hydrogen atom and of the possibility of interlocking between neighbor lattice molecules, it would be well to define clearly just what we intend the expression "size of an atom" to mean.

Definition of Radius of Atomic Domain

The size of an atom, or molecule, will depend on the nature of the experimental probe which is used in its exploration. An atom which appears to be of a certain size under one set of conditions may present itself quite differently in another situation. Thus, for example, has arisen the well-recognized distinction between the "gas kinetic radius" and the "crystal radius" of an atom. Such a difference is not only to be expected on theoretical grounds, but is fully supported by a comparison of atom sizes actually obtained under different experimental conditions. The meaning of the expression "the size of an atom" is therefore ambiguous, unless the circumstances of the determination are defined. In the present paper we are interested in the size of hydrogen atoms under the conditions existing in the crystal lattice. This means that we are concerned with the size which the hydrogen atom (on a molecule) possesses in collision with hydrogen atoms on the surfaces of neighbor molecules, as a result of thermal motions which these molecules are undergoing, generally vibration, although sometimes also rotation.[6]

[4] Since the manuscript of this article was submitted for publication, two other papers have appeared which indicate that the benzene ring is really the flat graphite ring: "An X-ray Analysis of the Structure of Hexachloro benzene, etc.," Mrs. Lonsdale, *Proc. Roy. Soc.* (London), **A133,** 536 (1931); and "The Molecular Association, The Apparent Symmetry of the Benzene Ring, etc.," Hendricks and Hilbert, THIS JOURNAL, **53,** 4280 (1931).

[5] Mrs. Lonsdale, *Proc. Roy. Soc.* (London), **A123,** 494 (1929).

[6] Pauling, *Phys. Rev.*, **36,** 430 (1930).

Gas Kinetic Radius.—We may attempt to represent the geometrical factors of a typical gas collision by Fig. 1. H represents a hydrogen atom bonded chemically to a carbon atom C, which in turn is connected to the other atoms in the molecule of which it is a part. The distance between the two nuclei C–H is about 1.08 Å. This may be calculated from the moment of inertia 5.17×10^{-40} for methane.[7] About the same value, 1.08 Å., is also readily calculated from the smallest moment of inertia found by Patty and Neilsen[8] for formaldehyde, namely, about 2.7×10^{-40} for the rotation of the molecule $\overset{H}{H}>C=O$ about the horizontal axis. This distance of separation of the nuclei of the two atoms is likely to remain approximately the same for methane molecules in the solid, liquid and gaseous states, and over a considerable temperature range, because of the difficulty of exciting vibration along the C–H bond, and this distance is also likely to hold for a hydrogen bonded to aliphatic carbon in *any* organic molecule.

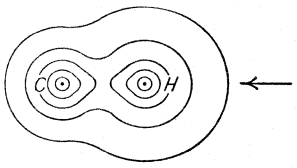


Fig. 1.

In accordance with the somewhat vague picture fostered at the present moment by the quantum mechanics, the two electrons of the electron pair which holds the two nuclei together, one electron supplied by the hydrogen and the other by the carbon, one electron with a right-handed and the other with a left-handed spin, are circulating around both nuclei, throughout both atomic domains, but spending a large share of their time, because of the eccentricity of the virtual orbits, between the two nuclei. The distribution of the electron density in such a system possibly resembles somewhat that calculated by London[9] for the hydrogen molecule, and may be represented by the contour lines shown in Fig. 1. The positions of these contours given in the present figure are not to be considered the true ones, which must wait upon the actual calculation, but as merely indications of the fact that the electron density is greatest near the central portions of the system, and from there grades off exponentially toward the outer regions of the atomic domain. In a certain sense, then, the atomic domain of the hydrogen may be said to extend out from the nucleus to a very large distance, indeed to an infinitely large distance.

Now, when another molecule approaches from the direction indicated by the arrow, presenting one of its hydrogen atoms so that collision will occur with Hydrogen Atom H of Fig. 1, the two approaching hydrogen atoms first interact to develop an attractive force, the so-called van der Waals force. As the approaching hydrogen atom is carried deeper into

[7] Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

[8] Patty and Neilsen, preliminary report in the Am. Physical Society Program Bulletin for the Cleveland Meeting, **5**, 24 (1930).

[9] London, *Z. Physik*, **46**, 455 (1928).

the contours of Atom H, a mutual repulsive force begins to make itself effective. Rebound will finally set in, and the visitor atom will be driven elastically back out of the reach of the field of Atom H. Thus we may define the gas kinetic radius by dividing the distance of closest approach of the two hydrogen nuclei (one of which is shown in Fig. 1) by 2, and, taking this distance as radius, circumscribe two virtually hard spherical shells about the two nuclei, so that the two shells touch at the mid-distance. The depth of penetration, and hence the atomic domain radius, will depend on the violence of the impact blow; the radius would be expected to *become smaller as the temperature increases*, and in general will be smaller for a gaseous collision than for a solid or liquid.

Crystal Radius.—In a crystal the momentum of the approaching hydrogen atom is the momentum of the molecule to which it is rigidly attached, and the motion of the molecule is a vibration of the molecule as a whole about an average position within the lattice. As the approaching molecule moves out of its average position to approach Atom H, the blow against Atom H is very greatly softened because an attractive force seated in a neighbor molecule on the other side of the vibrating molecule slows it down, in the same way that a pendulum is slowed down after it passes through the bottom of its swing. In a gaseous collision, on the other hand, there is no source of attraction to hold the approaching molecule in check, and its blow of impact is delivered in full force. An organic crystal which is warmed up through a considerable temperature range suffers an expansion of its lattice to accommodate the increasing amplitude of the thermal vibration of the molecules with more free space or co-volume, and even as fairly low temperatures it is to be supposed that some free space will exist. It is therefore to be expected that the crystal radius, in contrast with the gas kinetic radius, will *increase with increasing temperature.*

Figure 2 diagrams the situation. A and B represent the framework of two lattice molecules vibrating about their average positions. When the two hydrogen atoms H_A and H_B move far enough toward each other, due to the motion of A and B, to which the hydrogen atoms are attached, repulsive forces cause them, and consequently also A and B, to retreat. On the other hand, when the molecules A and B recede beyond their average positions, the hydrogen atoms are pulled back together by attractive forces. We may define the crystal radius as half of the *average distance* between the hydrogen nuclei.[10] This definition of atomic domain radius in crystals will also hold approximately for the domain radius of atoms on the

[10] If this picture of the spacing of molecules in a lattice is pushed to its logical conclusion, it is to be noted that over the whole temperature range in which the lattice is stable, even at the absolute zero (because of the zero-point energy), the molecules will never occupy true equilibrium positions, that is, positions at which the repulsive and attractive forces balance, but will be occupying average positions. In the average positions the hydrogen atoms will be attracting one another.

surface of a liquid molecule. To adopt such a definition of atomic domain in the case of two vibrating neighbor molecules in a crystal lattice is, of course, begging the question of the space gaps between neighbor molecules which we have set out to answer, unless the particular size of hydrogen atom domain which is employed can be justified independently or unless the particular size which will explain the spacing of this molecule along one crystal axis will also account for the spacings along all other axes of the same crystal and along all axes of all other crystals in which the H . . . . H contact is involved.

The electron density contours of the hydrogen atoms of Fig. 2 may be thought of as being compressed on approach, and as expanding on recession, like two balloon surfaces always in contact; or they may be thought of as undergoing a penetration into one another, as shown in the figure. In the present paper we fortunately need not concern ourselves with this precise mechanism, or with the origin and mechanism of the attractive and repulsive forces, since *the intention is to approach the problem in a purely empirical manner, to determine whether the spacing of organic molecules in crystal lattices can be explained in terms of atom domains of constant size in the same way that the spacing in inorganic crystals is at present accounted for in terms of ion domains of substantially constant radii.*

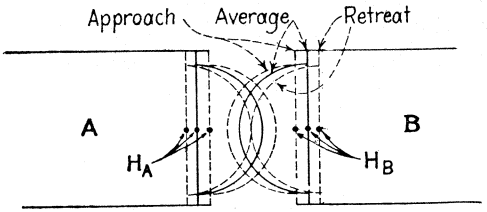


Fig. 2.

It is extremely convenient to describe the positions and spacings of the molecules with respect to one another by means of drawings and three-dimensional lattice models. For this purpose it is almost essential to represent the outer regions of the atom domain as a hard surface, and, since there is good reason for believing that the atom domain possesses approximately spherical symmetry, we shall employ a hard spherical surface. To call an atom a hard sphere is, admittedly, using a figure of speech. But if we recognize that it is figurative language, no harm is done and much advantage is gained in the simplicity and usefulness of the conception for the purposes of model building.

It is now possible to proceed with the estimation of the actual size of the hydrogen atom domain. It will be done first for a gaseous molecule, and then it will be shown that a reasonable extrapolation to a larger size will give a hydrogen atom crystal domain which will account consistently for the spacings of organic molecules in a crystal lattice. To complete the argument it would be desirable to compute the radius of the hydrogen atom domain on liquid molecules; but the difficulty of knowing the precise packing of the molecules in the liquid state and of allowing for the free

space arising from the probably more or less chaotic orientation of the molecules, seems to make the computation impossible in most cases. The situation of oriented molecules in the monomolecular oil film may eventually afford the opportunity of making such a computation, but at present our ignorance of the nature of the lateral packing and interlocking of the hydrocarbon chains does not encourage the attempt.

Empirical Estimation of Gas Kinetic Radius for Hydrogen.—The radius of the atomic domain of hydrogen bonded to carbon in a gaseous molecule may be obtained probably more easily from methane than from anything else. Rankine and Smith[11] have found from viscosity measurements, and by calculation with Chapman's equation, that the collision area of methane is 7.72 sq. Å. In so far as the Sutherland model is not valid, and to the extent to which Rankine and Smith's value is not reliable because of the small temperature range of the viscosity measurements (only from 17 to 100°), our own calculation of the atomic domain will be in error. The value is probably substantially correct, and at any rate is good enough for our present needs.

In a gaseous encounter with another like molecule, a molecule of methane probably presents itself as a sphere of revolution. The reasons for believing that this is so are as follows.

From the principle of the equipartition of energy the energy, E, of rotation of the methane molecule about a single axis is $^1/_2\ kT$, where k is the Boltzmann constant and T the absolute temperature. If, at let us say 25°, we assume that the equilibrium partition of energy is attained, $E = 2.04 \times 10^{-14}$ ergs. From the equation $\nu = \sqrt{2E/I}/2\pi$, where I is the moment of inertia, the frequency of spin ν may be calculated to be about 1.42×10^{12} r. p. s., and the time for one complete revolution to be about 7×10^{-13} seconds. Since both colliding molecules may be thought of as spinning simultaneously about four three-fold symmetry axes, or about three rectangular axes, and, furthermore, since the molecule would only have to execute about one-sixth of a revolution, it would behave effectively as a sphere if allowed a time not less than about 0.2×10^{-13} seconds. During such a time interval the translatory velocity of the bombarding molecule would carry it through a distance on the average of only about 0.14 Å.

If we further neglect any possible acceleration of velocity as the two molecules approach each other,[12] due to the attractive van der Waals forces, and any possible orientation as they get into one another's field, it is not likely that the approaching molecule would be able to penetrate appreciably into the spherical envelope of the molecule undergoing attack in regions where the hydrogen atoms do not happen to be at the instant of impact.

[11] Rankine and Smith, *Phil. Mag.*, **42**, 615 (1921).

[12] Herzfeld and Smallwood, Taylor's "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, Chapt. IV, Vol. I, p. 241.

It therefore seems difficult to escape the conclusion that the spinning molecule is able to guard its envelope of revolution against invasion, and that it will present itself almost as a total sphere (Fig. 3). If this is true, the collision area of such a sphere would be Rankine's value of 7.72 sq. Å., with a radius of 1.57 Å. Since the distance from the carbon nucleus to a hydrogen nucleus is 1.08 Å., the radius of the atomic domain of hydrogen beyond the nucleus would be about 0.50 Å. (0.49 Å.). This is the minimum size: it may be slightly larger, to an amount depending on the extent to which the methane molecule behaves as a partial rather than a total sphere of revolution.[13]

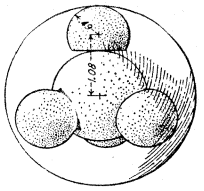


Fig. 3.

Empirical Crystal Radius for Hydrogen.—In view of what has already been said it is now reasonable to expect to find the crystal radius for hydrogen atom domain to be very much larger than the gas kinetic radius. Such an increase in domain size in passing from the gaseous through the liquid to the solid state is very likely to be a perfectly general behavior, characteristic of all atoms. For example, Natta and Nasini have recently shown that the xenon atom,[14] crystallizing in a face-centered cubic lattice, has a radius of 2.18 Å., whereas the gas kinetic radius[15] is 1.70 Å. For krypton the radius in the crystal is reported to be 1.98 Å.[16] and 2.04 Å.,[15] in a face-centered cubic lattice, while the radius in the gas is about 1.55 Å. For argon the respective crystal and gas radii are 1.92 Å.[17] and about 1.44 Å.[18] Approximately the same ratio holds for neon, and the same effect can be readily demonstrated for chlorine, bromine, iodine and other atoms.

Thus it will be noted that the crystal domain radius is larger than the gas kinetic radius by a factor of about $^4/_3$ or $^5/_4$ for the rare gases; the factor is 2 or more for hydrogen in the C–H group, for in the following sections the crystal lattice data indicate hydrogen atom domain radii of about 1.165 Å. (at about −195°) and 1.29 Å. (at room temperature), as compared with about 0.50 Å. for the gas kinetic radius. The hydrogen radius would seem to depend to some extent on the nature of the atom to which it is bonded. For example in crystalline H_2 (hexagonal close-packed and assuming rotating molecules) it is necessary to assign a value of about 1.5 Å. to the radius. In the present paper, however, we are interested only in hydrogen bonded to carbon. It is to be noted also that the crystal radius of hydrogen may be reduced by rotational rubbing.

[13] The problem of collision between rotating molecules has been treated by Pidduck, *Proc. Roy. Soc.* (London), **A101,** 101 (1922); and by Chapman and Hainsworth, *Phil. Mag.*, **48,** 593 (1924).

[14] Natta and Nasini, *Nature*, **125,** 457 (1930).

[15] Nasini and Rossi, *Gazz. chim. ital.*, **58,** 433 (1928).

[16] Keesom and Mooy, *Nature*, **125,** 889 (1930).

[17] Simon and Simson, *Z. Physik*, **25,** 160 (1924).

[18] Rankine and Smith, *Phil. Mag.*, **42,** 601 (1921).

Crystalline Methane.—Mooy, whose results are undoubtedly more reliable than those of McLennan and Plummer,[19] has recently shown by x-ray[20] examination of methane at liquid nitrogen temperature that the molecules are cubic close-packed in a unit cell of 5.88 Å. edge length. Pauling, basing his argument in part on heat capacity data, has demonstrated that the methane molecules are almost certainly rotating in the lattice above 20°K. (−253°). These effective spheres of revolution, without points of strong attraction for their neighbors, would be expected to pack together, as they do, in a face-centered cubic lattice, just as do the spherically symmetrical argon, krypton and xenon atoms.

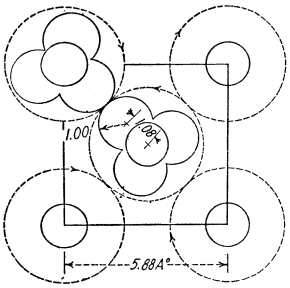


Fig. 4.

The x-ray analysis shows, of course, the positions of the carbon atoms only. The space gaps may be filled up so that the spheres of revolution osculate in the lattice, as shown diagrammatically in Fig. 4, by attaching hydrogen atoms to the carbon atoms at tetrahedral angles, with a C–H internuclear distance of 1.08 Å., and a hydrogen atom domain of radius 1.002 Å. This radius, probably reduced to the given size by rotational rubbing against neighbor molecules, would be expected to be somewhat larger if the molecules were not rotating. Perhaps some "cog-wheel" rotation occurs.

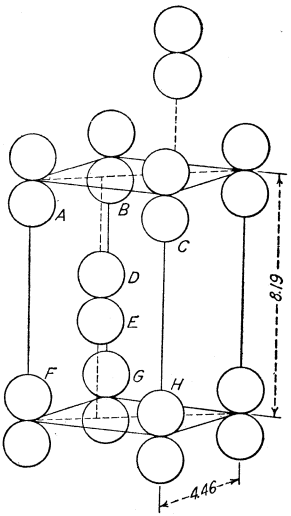


Fig. 5.

Crystalline Ethane.—Mark and Pohland[21] have made an x-ray examination of crystalline ethane, using the powder photograph method, also at liquid nitrogen temperature (−195°), and report the hexagonal structure shown in Fig. 5. (This figure is similar to one given in Hendricks' review.) The carbon atom pairs in the figure are the C–C atoms of the C_2H_6 molecule. Now, if hydrogen atoms of size a little larger than that in methane, namely, with atomic domain radius of 1.165 Å., are attached to the carbon atoms at tetrahedral angles and with C–H internuclear distance of 1.08 Å., the space gaps are all filled up, so that the *hard spherical surfaces of the hydrogen atom domains of neighbor molecules just kiss*, on the supposition that the molecules

[19] McLennan and Plummer, *Phil. Mag.*, **7**, 761 (1929).

[20] Mooy, Dissertation, *Nature*, **127**, 707 (1931); *Proc. Acad. Sci. (Amsterdam)*, **34**, 550 (1931).

[21] Mark and Pohland, *Z. Krist.*, **62**, 103 (1925).

are not rotating. Figure 6, which is a photograph of a three-dimensional model made to scale, shows the manner of the interlocking. This hydrogen atom size accounts exactly not only for the horizontal edge length of the unit cell, 4.46 Å., but also for the vertical height, 8.19 Å. The hexagonal symmetry of the lattice is most beautifully accounted for in terms of the interlocking of the molecules, which themselves possess hexagonal symmetry, as is clearly to be seen from the photograph of the model, and also from Fig. 7, which presents a view from above. Every ethane molecule in the body of the lattice makes six double contacts with its six immediate neighbors, contacts which resemble the meshing of teeth in gears.

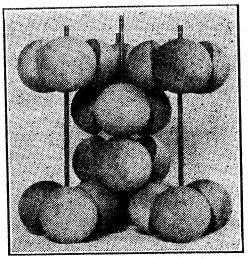


Fig. 6.

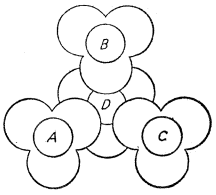


Fig. 7.

It is of course possible that the molecules are rotating in the lattice about their own vertical axes. The hydrogen domain radius would then be about 0.96 Å., approximately the same as in methane, and is to be thought of as reduced to this size from 1.165 Å. by rotational rubbing. Possibly the rotation is more or less of a "cog-wheel" type. On the whole perhaps the non-rotating molecule solution is more satisfying, but both solutions seem possible stereochemically, and the question of whether the molecules are really spinning or not below the melting point of crystalline ethane will have to be determined by some independent method.

Crystalline Hexamethylenetetramine, $(CH_2)_6N_4$.—Figure 8 is the well-known diagram of the arrangement and spacing of the hexamethylenetetramine molecules in the body-centered cubic lattice, worked out by x-ray analysis by Dickinson[22] and Raymond. Inspection of the figure shows the large space gaps between neighbor molecules. The spacing of the molecules is determined by contact between the missing hydrogen atoms along the cube edges. Such a contact is illustrated in Fig. 8 by the insertion of Hydrogen Atoms, a, b, c, d to complete the two methylene groups. (The carbon atoms are represented by the solid black circles.)

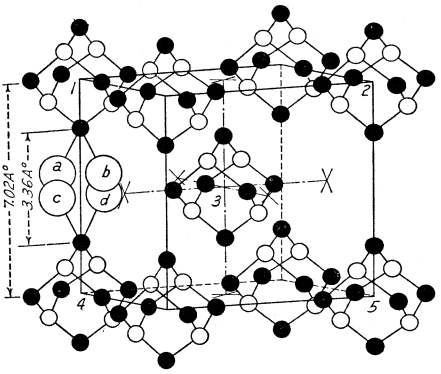


Fig. 8.

[22] Dickinson and Raymond, THIS JOURNAL, **45**, 22 (1923); and Mark, *Z. physik. Chem.*, **107**, 181 (1923).

If hydrogen atoms of crystal radius 1.29 Å. and with C–H internuclear distance of 1.08 Å. are now attached to the carbon atoms, distant 3.36 Å. from one another, the unit cube edge 7.02 Å. is precisely accounted for. The radius 1.29 Å. may be thought of as being assumed *ad hoc* or as derived empirically; but this same radius will now account extraordinarily satisfactorily for the spacings along all axes of all other crystals (where H . . . . H contacts are involved and at room temperature) so far studied by the author. This is the radius which will be used in the stereochemical solutions of aromatic molecule lattices in the following pages.

The molecules also contact along the cube diagonals. Figure 9 is a diagonal plane section through the cube from one edge to the edge opposite; two of the cube diagonals lie in this plane, running from 1 to 5 and from 2 to 4, in the figure. The carbon atoms, diameter 1.54 Å., are represented by the solid black circles, the nitrogen atoms by the systems of concentric rings and the hydrogen atoms by the large single circles. Hydrogen Atom A of Molecule 3 (the middle molecule) kisses the nitrogen atom of Molecule 4 in the plane of the paper; and Hydrogen Atom B, which is somewhat forward of A, and a third hydrogen atom lying directly behind B, and deeper than A into the plane of the paper, both also kiss the nitrogen atom. *Thus the domain of the nitrogen atom on Molecule 4 rests in a nest of three hydrogen atoms belonging to the neighbor Molecule 3, with the triplicate contact centering along the cube diagonal.*

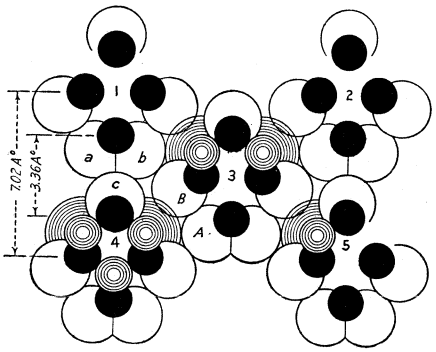


Fig. 9.

The radius of the nitrogen atom domain which will permit contacts of this sort is about 1.5 Å. A nitrogen atom, with five valence electrons, uses only three in bonding itself chemically to the three carbon atoms to which it is linked in the hexamethylenetetramine molecule, and accordingly is left with a residuum of two unshared electrons. It is entirely reasonable to suppose that these two electrons will form an atomic "bulge" or projecting domain considerably larger than the hydrogen atom domain. More quantitatively, 1.5 Å. is about the domain radius size which one would expect the nitrogen atom to possess, in view of the fact, already noted, that atoms in general will exhibit a larger domain in crystals than in gases, and in view of the further fact that in order to account for the collision area of the gaseous ammonia molecule, 6.40 sq. Å. (reported by Rankine),[23] on the assumption that the molecule has a tetrahedral shape,

[23] Rankine, *Phil. Mag.*, **42**, 613 (1921).

nitrogen atom at the top and the three hydrogen atoms at the base, with a moment of inertia of 2.78×10^{-40} (reported by Robertson and Fox),[24] it is necessary to assign the nitrogen atom domain a radius size of about 1.2 Å. in the gaseous state. The ratio 1.5:1.2 for the crystal and gas radii is about the same as for the rare gases.

Hence it seems very probable that every molecule in the lattice partakes in eight such contacts, as illustrated by Molecule 3 in Fig. 9, two contacts along every one of the four diagonals of the unit cell. The spacing and symmetry of the lattice are thus accounted for in a most satisfactory manner, both along the cube edges and diagonals of the unit cell, in terms of the dimensions and symmetry of the molecule.

A Proposed New Feature of Structure for the Benzene Ring.—In spite of the large number of proposals of benzene molecule structure that have been made in classical organic chemistry and the more recent accretions to the list, the disposition of the fourth bond of the carbon atoms is still a baffling problem. x-Ray analysis is beginning to indicate quite clearly, as has already been noted on a previous page, that the unsaturated benzene "ring" is indeed a six-carbon atom ring and that the ring is flat, like the graphite ring rather than the "puckered" ring of diamond, although the saturated cyclohexane ring may be puckered as in diamond or as in the camphor molecule.

Not long ago Pauling made a most interesting suggestion that the fourth electron of every carbon atom is circulating,[25] in so-called μ-orbits, across the flat ring and around the carbon atom nucleus in the para position, thus forming chemical bonds connecting the para carbon atoms; but in a more recent paper he[26] suggests the possibility that every carbon atom is connected to one neighbor carbon by two single bonds and to the other by a double bond, and explains away the susceptibility to chemical addition, which is to be expected from such an unsaturated structure, by supposing that there is oscillation of the double bonds from one position to another, a supposition which in terms of the quantum mechanics would probably lead to chemical stability. At any rate it now appears, in apparent default of decisive chemical evidence to render judgment among the claims of the various benzene structure theories, that we may not be unduly optimistic to hope for an early solution of the difficulty either by means of x-ray intensity measurements, or even perhaps at the hands of the quantum mechanics.

But, in the meantime, whatever the answer to the question of fourth bond disposition may eventually be, it would seem abundantly clear that the unsaturation of the benzene ring manifests itself in the form of a pro-

[24] Robertson and Fox, *Proc. Roy. Soc.* (London), **A120**, 189 (1928).

[25] Pauling, THIS JOURNAL, **48**, 1132 (1926).

[26] Pauling, *ibid.*, **53**, 1367 (1931).

tuberance or "bulge," extending out perpendicularly from each face of the flat ring. This idea may be said to be strongly supported by empirical evidence. As the idea developed in the author's mind it was at first supposed that the bulge might take the form of a crater-like elevation protruding above and below the carbon ring; then that the bulge might be cone-like, with the summits above and below the center of the ring; but finally that it must take the form of hemispherical domes, with a dome on each face of the ring. This dome is to be thought of as an electron domain, analogous to the domain of the hydrogen atom and the nitrogen atom, already discussed in preceding pages. The space occupied by this dome domain is guarded more or less against invasion by approaching atoms and molecules depending on the violence of the impact below. The best evidence for the existence of the dome arises from the possibility of explaining quite satisfactorily the observed manner of the spacing and packing of aromatic molecules in crystal lattices, if such a dome is assumed to be present, and the apparent difficulty of so doing without the dome.

In the present paper, while we are primarily interested only in the empirical evidence supporting the idea of the presence of the dome, it may be noted, in passing, that a seemingly sound theoretical justification for the idea is to be found in Pauling's first proposal of benzene ring structure. His virtual electronic μ-orbits, encircling para carbon atoms, would be expected to repel one another, and to flare out symmetrically from both faces of the ring to give effectively two hemispherical domes.

Now we may proceed to the proposed stereochemical solutions of graphite, anthracene and naphthalene, benzene and hexamethylbenzene; then some additional arguments for the presence of the benzene dome will be presented.

Structure of Graphite.—x-Ray analysis has now shown without doubt that the carbon atoms of graphite are arranged in flat hexagonal rings in flat layers, in contrast to the puckered layers of diamond. These flat layers are superimposed above one another, but are separated from one another at a surprisingly large distance[27] (3.40 Å.), a structure for which it has hitherto been difficult to find a satisfactory explanation. Such a large distance between these molecule layers certainly strongly suggests the presence of protuberances perpendicular to the flat layers, that is, to the faces of the hexagonal rings. It is these protuberances which hold the layers apart at the observed spacing.

Figure 10 shows the nature of the suggested structure. Every hexagonal graphite ring possesses a hemispherical dome on each of its two faces, with a dome domain radius, measured from the mid-point of the ring, of about 1.84 Å. This dome radius is considerably smaller in graphite than

[27] Hassel and Mark, *Z. Physik*, **25**, 317 (1924); Bernal, *Proc. Roy. Soc.* (London), **A106**, 749 (1924).

in benzene, as will be seen later, because in the graphite structure every carbon atom is a part of three different rings, and must share its fourth electron among three different domes. Thus every graphite ring can claim only two electrons for the formation of its two domes, whereas benzene builds its two domes from six electrons. A dome in one layer fits into a nest of three domes in the adjacent superimposed layer, and this relative arrangement of superimposed layers explains exactly the relationship deduced from x-ray analysis. In the observed arrangement a six-carbon hexagon in one layer is so placed that three of its carbons (all in meta positions with respect to one another) lie directly above and below carbon atoms in adjacent horizontal layers, and the other three carbons (also in *meta positions*) lie directly above and below the centers of rings in adjacent layers. Furthermore, while the carbon atoms within a flat layer are held together by chemical bonds, the interlayer forces, by virtue of the contacting between the electron domain domes, are merely van der Waals forces. Hence these layers would be expected to be susceptible to slippage and gliding with respect to one another, in a manner which accords with the facts.

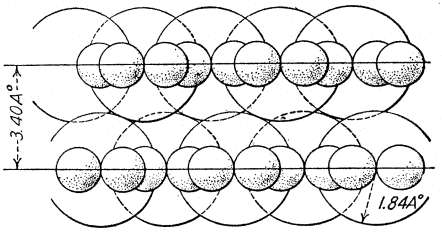


Fig. 10.

Anthracene and Naphthalene.—In Sir William Bragg's[28] original examination of crystals of naphthalene and anthracene, and even in Robertson's more recent analysis,[29] it was supposed that the carbon rings in the two molecules were puckered diamond rings. But, still more recently, in a letter to *Nature*, Banerjee[30] presents what is undoubtedly just about the correct solution of these crystal structures, and his analysis shows that the carbon rings are flat, and further differs from the solutions of Bragg and Robertson in placing the flat faces of the molecules more nearly in the *bc* than in the *ac* planes. In the same number of *Nature* Robertson admits the essential correctness of Banerjee's conclusions and also presents reasons based on unpublished work of his own and of Bragg in further support of these conclusions. Banerjee was apparently able to make his successful analysis because of the work of Bhagavantum on the magnetic anisotropic properties of naphthalene. Bhagavantum,[31] taking advantage of the peculiarly strong magnetic susceptibility of the benzene ring in a direction perpendicular to its flat face, suspended small crystals from silk fibers in a strong magnetic field, and from the position assumed by the

[28] Bragg, *Proc. Phys. Soc.* (London), **34,** 1, 33 (1921); **35,** 3, 167 (1923).
[29] Robertson, *Proc. Roy. Soc.* (London), **A125,** 542 (1929).
[30] Banerjee, *Nature,* **125,** 456 (1930).
[31] Bhagavantum, *Proc. Roy. Soc.* (London), **A124,** 545 (1929).

crystals in the field deduced the placement of the naphthalene and anthracene molecules with respect to the crystal axes of the lattice. With this much of a guide to the probable parameters of the individual carbon atoms, Banerjee very cleverly obtained a good match between calculated and observed x-ray intensities, thus establishing an extremely probable structure.

According to Banerjee, "the correct positions of the molecules are obtained by first placing them along the *bc* planes, then rotating them through 25° about the *c* axis (the two molecules in the unit cell being rotated in opposite directions), and then rotating them about *b* axes through 12 and 9° for naphthalene and anthracene, respectively." This statement together with the cell dimensions and space group will be taken as the basis of our stereochemical solution.

Since the molecules of any lattice normally arrange themselves so that the maximum number of contacts between atoms attracting one another with van der Waals forces is obtained, and the minimum possible potential energy achieved, we should expect the molecules of anthracene, for example, to pack together face to face, with the ten hydrogen atoms of one molecule contacting with the ten of a neighbor molecule. But since the presence of the dome-like protuberance on the faces of the rings prevents as close a packing as this, just as it does in the case of graphite, the molecules have to be content with the next closest possible packing, which would seem undoubtedly to be the one described by Banerjee.

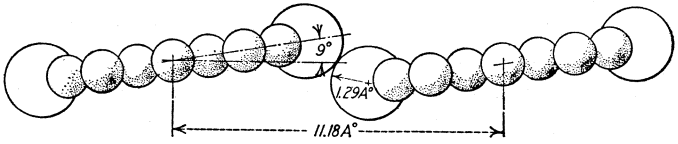


Fig. 11.

The dimensions of the anthracene monoclinic unit cell are: $a = 8.58$, $b = 6.02$, $c = 11.18$ Å., $\beta = 125°$. The space group is C_{2h}^5. Let us consider Fig. 11, where two anthracene molecules (with the domes temporarily omitted) are inclined to the *c* axis at an angle of 9°, in accordance with the specifications of Banerjee. The distance between molecule centers is 11.18 Å. (length of *c* axis). The three rings of the anthracene molecule are graphite rings with carbon atom diameters of 1.42 Å. The hydrogen atoms are placed in the plane of the rings, with a C–H internuclear distance of 1.02 Å. This distance is reduced from 1.08 Å., the H-*aliphatic* C internuclear distance, to correspond with the analogous reduction observed from aliphatic C-*aliphatic* C (1.54 Å.) to aliphatic C-*aromatic* C (1.48 Å.). It cannot be in error by more than a few hundredths of an Ångström unit, and probably is just about right. In the figure there are contacts between

two end hydrogen atoms of one molecule and two of the other, although the second hydrogen atoms are hidden directly behind those shown in the drawing. With the molecules in the position shown, the hydrogen domain radius which just gives contact is 1.29 Å. In *naphthalene*, the *c* axis length is 8.68 Å., and when these two molecules, shorter than anthracene, are set along the *c* axis, with their centers at this distance apart, and with their end hydrogen atoms (radius 1.29 Å.) just kissing, the angle of inclination of the molecules to the *c* axis is 12°, which accords beautifully with Banerjee's requirement.

It is indeed difficult to represent clearly in two-dimensional drawings the details of these fairly complicated three-dimensional models. In Fig. 12, where we look into the *ab* face of the anthracene unit cell, we may avoid some confusion of lines by looking directly into the ends of the molecules rather than perpendicularly into the face. Such a view foreshortens the *a* axis, reducing it from 8.58 to 7.71 Å. In this figure the five molecules Nos. 1, 2, 3, 4, 5, the centers of which lie in the nearer *ab* face, have their carbon atoms shaded; the others, Nos. 6, 7, etc., which lie in the farther *ab* face, are unshaded. It will be noted that Molecules 1 and 2 (at the top) as well as Molecules 4 and 5 (at the bottom) are inclined at angles of 25° to the *bc* plane, and that when their centers are spaced 6.02 Å. apart, their three outlying side hydrogen atoms (two of which are hidden in the drawing directly behind the first) all just contact with three of a neighbor molecule, when the hydrogen domain radius is 1.29 Å. Molecule 3, which is located a little to the right of the face center, is rotated 25° clockwise, in contrast with the counter-clockwise rotation of Molecules 1, 2, 4 and 5. Of the three outlying hydrogen atoms on the lower right-hand side of Molecule 3, the one farthest to the front rides on the upper right-hand end hydrogen atom (farthest to the front) on Molecule 5, as shown at C. A similar contact in the next layer above is shown at C'. All three of these hydrogen atoms of Molecule 3 also ride on the domes of Molecule 5, although the domes are not drawn in Fig. 12. But the manner in which the side hydrogen atoms (not shown in Fig. 12) of Molecule 7 ride up on the domes of Molecule 8, which lies below Molecule 5, is clearly indicated in Fig. 13, which gives a view looking into the *ac* face. The size of the domes on anthracene is small enough to permit Molecule 7 to slip far enough to the

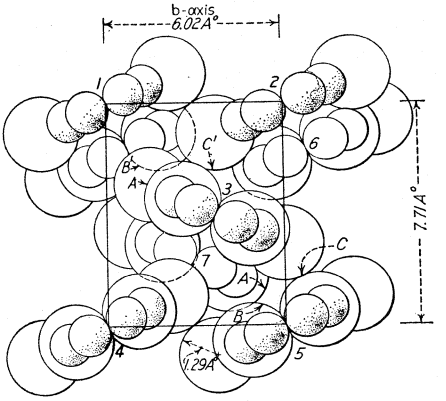


Fig. 12.

left (in Fig. 13) and far enough to the front (in Fig. 12) to let Hydrogen Atom A of Molecule 7 ride up on top of Hydrogen Atom B of Molecule 5. The same sort of contact occurs between Molecules 7 and 4 (Fig. 12). These hydrogen–hydrogen, and hydrogen–dome contacts between the oppositely inclined layers, repeated over and over again from layer to layer, account very satisfactorily for the observed spacings along the a axis. The angle β (125°) between the a and c axes is also quite exactly explained in terms of the contacts described.

The dimensions of the unit cell of naphthalene are: $a = 8.34$, $b = 5.98$, $c = 8.68$ Å., $\beta = 122°44'$. The arrangement of the molecules in the cell is almost identically the same as in anthracene. We have already accounted for the spacing along the c axis. The smaller a axis in naphthalene

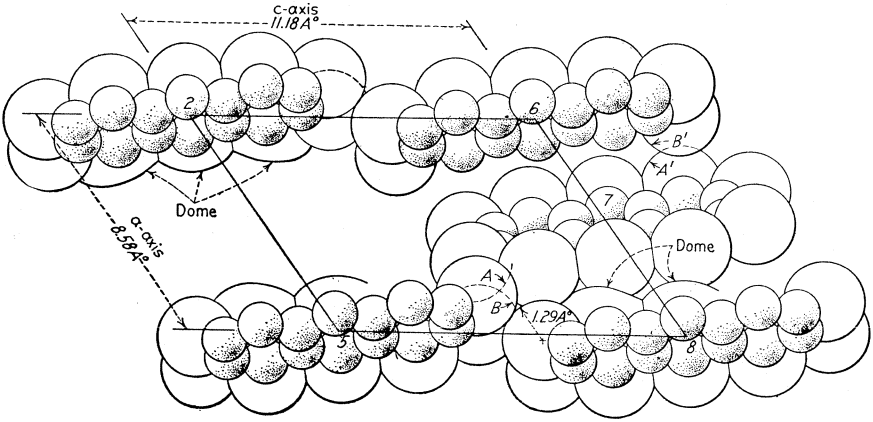


Fig. 13.

as compared with anthracene is to be attributed to the presence of a larger dome size at the two extremities of the naphthalene molecule as compared with anthracene. The domes over the middle ring of anthracene are distinctly small, probably not much larger than the graphite dome. At the extremities of the anthracene molecule the dome size becomes larger because there the fourth electrons do not have to be shared between the domes of an adjacent ring. To put the matter in most general terms, without attempting to give a detailed description of the exact size and shape of these domes, we may observe that in naphthalene we have ten electrons to distribute through the domes over two rings, whereas in anthracene we have only fourteen electrons to distribute over three rings. It is to be expected, then, that the dome size at the two extremities of the anthracene molecule would be appreciably smaller than in naphthalene. This larger dome in naphthalene prevents Molecule 7 (Fig. 13) from slipping quite as far to the left as it does in anthracene, and hence gives a smaller value of the angle β; and prevents Atom A from riding quite as high up

on Atom B (Figs. 12 and 13), and hence also reduces slightly the length of the a axis in the case of naphthalene. The b axes are almost exactly the same in the two crystals, but it is likely that the slightly different arrangement of the molecules in naphthalene results in tipping the molecules with respect to the bc plane (Fig. 12) slightly more than in the case of anthracene, enough to reduce the b axis from 6.02 to 5.98 Å.

It may be of interest to note that essentially the same stereochemical solution can be obtained, as far as spacing along the c axis is concerned, by employing the puckered diamond ring. However, along the b and a axes the staggering of the hydrogen atoms above and below the plane of the puckered ring is such that no consistent contacting between hydrogen atoms occurs. If the nature of the packing here suggested is accepted as correct, then the stereochemical argument strongly favors a graphite instead of a diamond ring.

Benzene.—Eastman,[32] Broomé,[33] Mark[34] and Cox[35] have subjected crystalline benzene to x-ray examination. All of the analyses agree roughly as to the orthorhombic cell dimensions. Probably Cox's results, obtained with crystals at $-22°$, are most reliable; $a = 7.44$, $b = 9.65$, $c = 6.81$, 4 molecules per unit cell and space group Q_h^{15}.

The stereochemical solution is shown in Fig. 14, looking into the ac face. The five shaded molecules, with their centers lying in the plane of the ac face, form a part of an end-centered lattice. At the opposite end of the cell, in the farther ac face, lying directly behind the shaded molecules of Fig. 14, is an exactly similar stack of molecules. In between these two lies a third similar stack, connecting the two together, but displaced in the lattice. In Fig. 14, the four unshaded molecules belong to this middle stack. On these unshaded molecules the domes have been omitted to avoid some confusion of line. This middle stack of molecules nestles into the nearer stack of the ac face and also into the farther stack, in such a way as to determine the length of the b axis (shown in Fig. 15) as well as the lengths of the a and c axes (Fig. 14). The details of this "nestling-in" are as follows. The farther end hydrogen atom of Molecule S′, in the lower right-hand corner of the cell (Fig. 14), supports the nearer

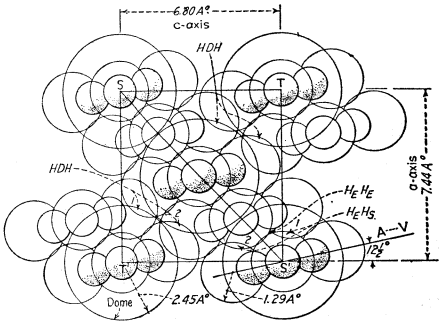


Fig. 14.

[32] Eastman, THIS JOURNAL, **46**, 917 (1924).
[33] Broomé, *Physik. Z.*, **24**, 124 (1923); *Z. Kryst.*, **62**, 325 (1925).
[34] Mark, *Ber.*, **57**, 826 (1924).
[35] Cox, *Nature*, **122**, 401 (1928).

end hydrogen atom of a molecule in the middle stack, as shown at H_EH_E. This type of contact is repeated over and over again from layer to layer up through the diagonal plane S'S. Also the farther end hydrogen of Molecule S' contacts perfectly with the nearer side hydrogen atom of the middle stack molecule as shown at H_EH_S, Arrow 1; and the nearer end hydrogen of the middle stack molecule contacts perfectly with the farther side hydrogen of Molecule S', as shown at H_EH_S, Arrow 2. In order to make these H_EH_S contacts perfect it is necessary to suppose that the benzene molecules are all tipped at an angle of $12^1/_2°$ to the *bc* plane, and they have been so drawn in Fig. 14. The H_EH_E and H_EH_S contacts are also illustrated in Fig. 15.

It is interesting to note that, when the molecules (Fig. 14) are tipped $12^1/_2°$ as just described, the two side hydrogen atoms on the left-hand side of the middle molecule of the nearer *ac* face (shaded) make a perfect contact with the dome of Molecule T', if the dome is assigned a radius of 2.45 Å., as shown at HDH, Arrow 1. And similarly the right-hand side hydrogen atoms of Molecule T contact perfectly with the dome of the molecule at the center of the face, as shown at HDH, Arrow 2. Thus these HDH, H_EH_E and H_EH_S contacts explain the spacings along the *a* and *c* axes. It will be noted that the side hydrogen atoms (radius 1.29 Å.) of Molecule S' do not contact with the side hydrogen atoms of Molecule T' along the horizontal axis, as was the case in naphthalene and anthracene.

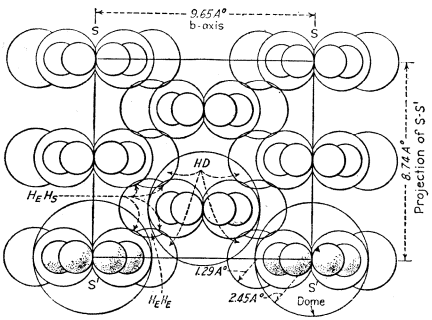


Fig. 15.

In Fig. 15 we are looking into the *ab* face, but in order to simplify the drawing we are not looking normally into the face but into the Section SS' (see Fig. 14), into the plane of the molecules themselves, that is, along the line A . . . . V (see Fig. 14), at an angle $12^1/_2°$ to the *bc* planes. This stereochemical solution accounts for the symmetry and all of the dimensions of the unit cell down to the last hundredth of an Ångström unit. The only further *ad hoc* assumption that must be made, except for the radius 2.45 Å. for the dome, is that the dome is very slightly deformable near the carbon atoms of the benzene ring, so that the end hydrogen atoms of neighbor molecules can penetrate a little into the spherical domain, as shown at HD in Fig. 15. Such a penetration is quite reasonable, since the hydrogens enter between the carbons, and can be thought of as slipping in between the ridges of Pauling's μ-orbits.

In concluding our discussion of the benzene lattice it may be pointed out that the stereochemical solution suggested here gives four molecules

per unit cell, strongest reflections for the 111 plane (as observed by Cox) and space group Q_h^{15} with the four molecules of the middle stack (Fig. 14) displaced somewhat, however, out of the face centers. As in the cases of naphthalene and anthracene, the puckered ring does not yield a satisfactory solution.

Hexamethylbenzene, $C_6(CH_3)_6$.—Mrs. Lonsdale's analysis[4] of the triclinic crystal hexamethylbenzene demonstrates the general features of structure shown in Fig. 16. This diagram gives a view looking into the *ab* face of a unit cell, where the *a* and *b* axes are inclined to one another at an angle of 119°34′. In this face the four corners are occupied by benzene hexagonal plane rings, made up of carbon atoms of diameter 1.42 Å., and in the figure numbered 1, 2, 3, 4, 5, 6. Attached to these at carbon bond

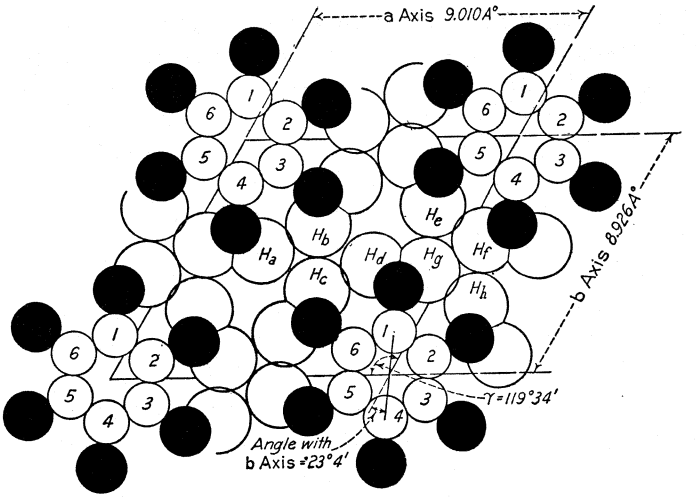


Fig. 16.

angles of 120° are the aliphatic carbon atoms (solid black circles) of diameter 1.54 Å., co-planar with the aromatic ring. The presence of large space gaps between the carbon atom clusters is evident from the figure. The question which we wish to have answered is: Can these gaps be filled up by attachment of the missing hydrogen atoms?

Regarding the methyl group Mrs. Lonsdale herself makes the following remarks. "In scattering power it is heavily weighted at the end nearer to the benzene ring by its carbon atom, which appears to retain its own electronic system more or less unchanged. . . . In fact the methyl group acts toward x-rays like an electronic shuttlecock, whereas single atoms behave rather like tennis balls. . . . Possibly if the exact shape and orientation of the methyl groups could be determined the problem of the crystal system would resolve itself into a question of the most convenient packing. . . . .

The easy distortion of the crystals by slipping about the crystallographic axes may be caused by the rolling of methyl groups upon one another."

Following out Mrs. Lonsdale's suggestion, one may now attach the missing hydrogen atoms of the methyl groups with the C–H internuclear distance 1.08 Å., as we have done in the case of the preceding *aliphatic* bonds. We must bear in mind, at this point, that Pauling has shown that the methyl groups in hexamethylbenzene are probably rotating,[6] at room temperature. With a hydrogen atom domain of 1.29 Å. radius no rotation could occur because of the interference of neighboring methyl groups (ortho positions) on the benzene ring, unless the violence of the rotation were sufficiently great to compress the atomic domains. This is probably just what happens. The collisions between the hydrogen atoms of rapidly rotating adjacent methyl groups resemble in many respects gaseous collisions. The momentum of the approaching hydrogen atoms would easily carry them rather deeply into one another's domain, probably without altering appreciably the nature of the rotation, thus allowing one methyl ring of revolution to roll against another. At the same time, the bumping of these rotating methyl groups against one another would be expected to produce a little bond bending, and in the supplementary stereochemical solution which we are offering here to account for the spacings actually observed by x-ray analysis, we are making the very reasonable assumption that the hydrogens of a methyl group, while maintaining their distance of 1.08 Å. from the carbon atom, are pushed together slightly, or, stated more exactly, that the normal tetrahedral angle (109°28′) between the line connecting a hydrogen atom to the aliphatic carbon and the line connecting the aliphatic to the aromatic carbon is distorted to an angle of about 125°.

In Fig. 10 the positions which the hydrogen atoms in the ring of revolution would occupy in the plane of the paper are shown. The rubbing of a methyl ring against a ring of *another molecule* would also be expected to reduce the atomic domain radius of the hydrogen atoms to some extent, and in the diagram the radius has been taken as 1.06 Å., reduced to this extent from 1.29 Å. by the impact of rotational collision. The reduction of the size of the hydrogen domain by rubbing between methyl groups on the *same* molecule is even more than this, to an extent illustrated in the drawing by the overlapping of Hydrogen Atoms H_c and H_d, H_g and H_h, etc.

The nature of the contact between methyl groups on vicinal molecules is clearly shown. Along the *b* axis, Methyl Group 1 makes a double contact with Methyl Groups 4 and 5 of the neighboring molecule, Hydrogen Atom H_g with Hydrogen Atoms H_e and H_f. Methyl Group 4 makes a double contact with Methyls 1 and 2.

We may now observe the lattice by looking perpendicularly into the *bc* face, Fig. 17. Since the 1–4 axis of the molecule is inclined 23°4′ to the

b axis (Fig. 16), we shall not be looking directly into Methyl Group 3, but shall be viewing it somewhat obliquely. It is extremely difficult to make the nature of the contacts, viewed in this direction, as obvious in a plane drawing as it is in a three-dimensional model of the lattice. But with

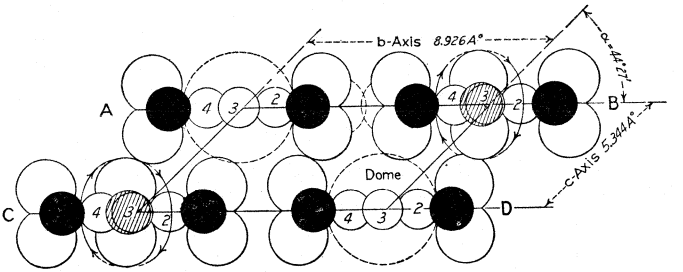


Fig. 17.

the aid of Fig. 17 and with the following list of the observed contacts, the general type of packing can be made fairly clear.

Upper layer	Lower layer
Methyl group 1 rolls on	Methyl group 5
Methyl group 2 rolls on	Methyl group 4
Methyl group 3 rolls on	Methyl group 2
Methyl group 4 rolls on	Methyl group 3 and Dome
Methyl group 5 rolls on	Methyl group 6 and Dome
Methyl group 6 rolls on	Methyl group 1

In these contacts made between molecules in the upper and lower layers, the hydrogen atom exhibits a domain radius approximately the same as in the *ab* plane, namely, 1.06 Å. Because of the presence of, and size of, the dome over the center of every benzene ring the molecules cannot pile directly over one another, center over center, and this is the reason, no doubt, why the crystal is not monoclinic or hexagonal. The lattice is triclinic because of the manner in which the Molecule A (Fig. 17) in the upper layer bridges the Molecules C and D in the lower layer.

In Fig. 16 it will be observed that the contacting between the spinning methyl groups of neighbor molecules along the *a* axis is almost, but not quite, the same as along the *b* axis, as indeed is to be expected from the slightly different lengths of the *a* and *b* axes. Dr. Pauling has very kindly suggested that this different spacing is controlled by the nature of the superposition of *ab* layers on one another. This is very probably the case. The spacing of the molecules in the *bc* stacks or nets is determined both by the rolling contact between methyl groups on vicinal molecules and by the nature of the bridging between layers, as already described. The different stacks of molecules along the *a* axes (Fig. 16) must then fit into one another as best they can. While the contacts along the *a* axes are good, and resemble quite closely those along the *b* axes, the contacts near the center of

the *ab* face are not so good. Here Atom H_b makes a single contact with Atom H_c, and Atom H_d just fails to touch Atom H_b, and H_a similarly fails to kiss H_c, or at least the interaction is looser than in the other contacts.

On the whole, this stereochemical solution for hexamethylbenzene has required more *ad hoc* assumptions than for the other crystals reported in this paper. But it must also be remembered that its structure is much more complicated than any of the others. In a later paper solutions of diphenyl, phenanthrene, indigo, *p*-dichloro-, dibromo- and di-iodobenzene, will be presented. In fact no crystal so far studied by this stereochemical method has failed to yield a reasonable and consistent result. With a little more experience in matching the stereochemical solution against the x-ray analysis, and with a more complete knowledge of the domain radii of oxygen and nitrogen and other atoms, it is probably not too much to hope that we shall be able to predict, accurately, the structural details of unit cells of organic crystals without x-ray analysis, simply from crystallographic and density data. At the very least, such a stereochemical approach should become an important aid, like Bhagavantum's studies on magnetic susceptibility, in determination of the parameters of the individual atoms in the skeletal organic molecules of the lattice.

Other Arguments for the Benzene Dome

In addition to the empirical crystallographic evidence already presented, we may marshal some further arguments in support of the postulate of the presence of an electronic dome domain over the face of the benzene ring.

1. **Collision Area of the Gaseous Molecule.**—Nasini and Lowry[36] have reported a collision area of 19.0 sq. Å. for the benzene molecule, determined by gaseous viscosity measurements. The satisfactory correspondence which one can obtain between collision areas of molecules in general and the collision areas predicted from a shadow-graphic treatment of probable models made to scale,[37] would seem to warrant an extension of this method of approach to the problem of gaining a decision among various disputed spatial configurations of organic molecules.

In the present case, a model of benzene made to scale (1 inch = 1 Å.) from a graphite ring, with six attached hydrogen atoms of *gas kinetic* radius about 0.63 Å. (taken as 0.63 instead of 0.50 Å. because probably *two* hydrogen atoms on each molecule on the average partake in the collision),[38] with a C–H internuclear distance of 1.02 Å., and with due consideration of the spins of the gaseous molecule gives a shadow area of

[36] Nasini and Lowry, *Proc. Roy. Soc.* (London), **A123**, 686, 692 (1929).

[37] Melaven and Mack, THIS JOURNAL, **54**, 888 (1932).

[38] Adam, *Proc. Roy. Soc.* (London), **A103**, 676 (1923); Adam, Berry and Taylor, *ibid.*, **A117**, 532 (1928).

just 16.0 sq. inches. This average area is much too small, and suggests strongly that the benzene molecule must certainly possess some structural feature which causes it to present a much larger target to molecular bombardment. When a hard-surfaced spherical dome is attached to each face of the ring, with a *gas kinetic* dome radius of about 2.0 Å. (reduced 20% from the crystal dome radius of 2.45 Å. by analogy with the similar reduction suffered by the rare gas atoms), the collision area comes out to be about 18.6. This is very good correspondence with the result of Nasini and Lowry. The argument is reasonable, and its force cannot be ignored.

2. Oil Films.—Adam[38] and his students, in their study of oil films made up of long chain molecules attached to polar heads which were phenol groups, with the molecules probably oriented vertically in the water surface, have found a surface area of 24.0 sq. Å. for every benzene ring in the condensed film, on the assumption, of course, that the OH group plays no part in the spacing. Since this film is reported to be a *solid* film, it would be very plausible to suppose that the packing resembles that of the end-centered lattice in the *ac* face of crystalline benzene, Fig. 14. The nature of the close-packing which we here propose for this film is illustrated in Fig. 18. The hydrogen atom dimensions (1.29 Å.) and the dome dimensions (2.45 Å.) are here exactly the same as in Fig. 14. It will be remembered that the lengths of the *a* and *c* axes in Fig. 14 are determined by the nestling in of the middle stack of benzene molecules. Here, in Fig. 18, the domes would be expected to pack together tightly, allowing the setting up of the system of perfect contacts between hydrogen and hydrogen, dome and dome, and dome and hydrogen pairs, shown in Fig. 18.

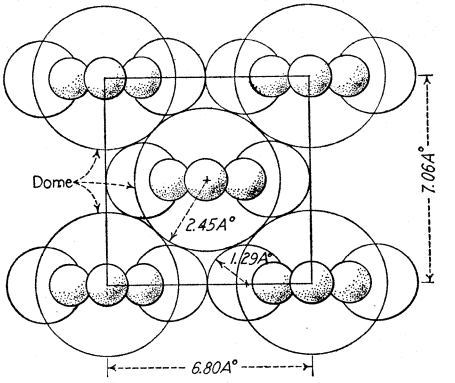


Fig. 18.

The author has considered various other possible packings, involving the hydrocarbon chains as well as the benzene rings, but cannot find any arrangement that is nearly as quantitatively satisfactory as this one. The film area of this unit rectangle, which contains two molecules, is exactly 48.0 sq. Å., giving 24.0 sq. Å. per molecule. The possibility of this arrangement and spacing depends, of course, on the presence of the dome. This argument for the presence of the dome would therefore seem to carry considerable force.

3. x-Ray Examination of Liquid Aromatics.—Stewart[39] has deduced from his x-ray examination of liquid benzene and other liquid aromatics

[39] Stewart, *Chem. Rev.*, **6**, 495 (1929).

some spacings of the order 4.7 Å., which he supposed to correspond with the thickness of the rings as they are packed together in the liquid state. But, as Adam[40] points out, it is difficult to account for such a large spacing in terms of the ordinary conception of benzene molecule structure. Such spacings can, quite evidently, be satisfactorily explained with the aid of the dome.

4. Molecular Domain Due to Unsaturation.—In general it is to be expected that unsaturation such as that of the benzene ring, or of a double bond, or of a triple bond, will manifest itself as a geometrically symmetrical bulge more or less impenetrable by approaching atoms and molecules. For example, Titani[41] has calculated from his gaseous viscosity measurements the collision areas (he expresses the results in terms of radii) of 10.63, 10.29 and 10.63 sq. Å., respectively, for molecules of ethane, ethylene and acetylene. These results obviously indicate, even when the spins are taken into consideration, that ethylene and acetylene, which in spite of their smaller number of hydrogen atoms and smaller internuclear C–C distances present about the same target area in collision as ethane, acquire considerable domain by virtue of their unsaturation. Very likely the acquired bulge is produced by the repulsion of the bonding electrons.[42]

In addition to the arguments given above, mention may be made of a curious x-ray diffraction effect which Raman observed when working with graphite.[43] It seems likely that this effect, as well as the peculiar magnetic[44] properties of the aromatic ring, may be related to the dome.[45]

And now, at the end, if it may be granted that the empirical evidence presented here constitutes a reasonably good case for the existence of the dome, there are certain implications which follow from the presence of the dome on the aromatic ring. For example, it becomes possible to make a

[40] Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 106.

[41] Titani, *Bull. Chem. Soc. Japan*, **4**, 277 (1929); **5**, 98 (1930).

[42] In this general connection it is possible to marshal the arguments of the Sugden parachor and the various treatments of liquid molecular volume to show the probability of a bulge on the benzene ring due to unsaturation. We shall, however, refrain from so doing because of the well-founded suspicion that such arguments, based on an application of the additive principle to skeletal organic molecules, are likely to be extremely misleading.

[43] Raman, *Nature*, **124**, 53 (1929).

[44] Raman, *ibid.*, **123**, 945 (1929); Ehrenfest, *Physica*, **5**, 388 (1925).

[45] Since the present manuscript was submitted for publication, Mrs. Lonsdale has published a paper (Ref. 4) in which she gives a map of electron density contours for hexachlorobenzene. It is exceedingly interesting to note that she does find a considerable electron density over the face of the benzene ring, and it seems quite possible to interpret the density distribution as being that which one would expect for a dome. There is a question, however, as to what interpretation can be put on the curious figure-8 shape of the contours over the center of the ring, if indeed the resolution of the analytical method is powerful enough to establish the form definitely.

calculation of the compressibility of graphite, and also of the compressibility of the single-layer phenol films studied by Adam. The working out of the Crum–Brown rule and its modifications is probably in part a matter of the steric hindrance of the dome. The benzene molecule is inert chemically because it is sheathed in the fairly impenetrable electron cloud of the dome. When a foreign atom or group does manage to displace a hydrogen atom under the dome-deforming influence of such a thing as a catalytic surface, for example, then the electrical character of the substituent itself, when it has entered the ring, will play a controlling role in the precise nature of the resulting distortion of the dome, and the resultant guarding and unguarding of the various positions around the ring. A detailed consideration of conclusions to which some of these implications lead must be left for a future paper.

The author wishes to express his gratitude to Dr. Preston M. Harris, and especially to Dr. Linus Pauling, for many helpful suggestions received during the preparation of this paper.

Summary

The problem of the space gaps between molecules in organic crystals and the interlocking of the molecules in the lattice is stated, and the question of whether the molecular spacing can be accounted for by contact between out-lying hydrogen atoms is considered.

The "size of atomic domain" is defined for the purposes of the problem, and the actual sizes of the hydrogen domain radius in the gaseous and crystalline states are derived empirically.

In terms of a probable hydrogen atom size the spacings of the molecules and the symmetry of the lattice are explained for crystalline methane, ethane and hexamethylenetetramine.

From a consideration of some aromatic crystal lattices there emerges a proposed new feature of structure of the benzene ring, namely, *a dome-shaped electronic domain protruding symmetrically from both faces of the flat hexagonal ring.* In terms of this dome a stereochemical solution of the spacing of the layers in crystalline graphite is offered, and in terms of the dome and a constant hydrogen crystal radius of 1.29 Å. explanations are offered of the lattice symmetry and molecular spacing of anthracene, naphthalene and benzene. An attempt is also made to give a stereochemical solution of the structure of the hexamethylbenzene lattice.

Further arguments are presented for believing in the existence of the dome, including the empirical evidence of collision area, oil films, x-ray examination of liquid aromatics and molecular volume.

COLUMBUS, OHIO

[CONTRIBUTION FROM PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.]

THE FLAME TEMPERATURES OF MIXTURES OF AMMONIA AND ITS PRODUCTS OF DISSOCIATION[1]

BY G. W. JONES,[2] BERNARD LEWIS[3] AND HENRY SEAMAN[4]

RECEIVED NOVEMBER 2, 1931 PUBLISHED JUNE 6, 1932

The United States Bureau of Mines has received many inquiries relative to the flame temperature of ammonia and its products of dissociation. Ammonia can now be manufactured rather cheaply and is being produced in such quantities that there are difficulties in finding an adequate market. The gas can be compressed in the liquid form in cylinders, and if it can be burned directly with air, or, if necessary, partially or completely cracked at the place where it is used, it may become of industrial importance as a heating, welding or cutting gas.

Ammonia decomposes according to the following reaction

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Completely "cracked" ammonia therefore consists of a mixture containing 75% of hydrogen and 25% of nitrogen.

The method of determining the flame temperatures was the same as described in previous publications,[5a,b,c] with certain modifications (described later) when ammonia was one of the constituents.

The Flame Temperature of Hydrogen–Nitrogen–Air Mixtures.—The flame temperatures of hydrogen–air mixtures have been measured[5c] and the maximum temperature was found to be 2045°. The flame temperatures of hydrogen–nitrogen–air mixtures were measured to determine the effect of adding nitrogen to the hydrogen–air mixtures. The results are shown graphically in Fig. 1. A mixture containing three volumes of hydrogen and one of nitrogen (representing completely cracked ammonia) has a maximum flame temperature of 1885°. The addition of this amount of nitrogen has therefore reduced the flame temperature about 160°. Incidentally, this temperature is approximately the same as the maximum flame temperature of methane or Pittsburgh natural gas in air.

Further additions of nitrogen depress the maximum flame temperature still more. For nitrogen and hydrogen in equivalent amounts it is 1680°,

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Physical Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[4] Junior Physical Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[5] (a) Loomis and Perrott, *Ind. Eng. Chem.*, **20**, 1004 (1928); (b) Jones, Lewis, Friauf and Perrott, THIS JOURNAL, **53**, 869 (1931); (c) Jones, Lewis and Seaman, *ibid.*, **53**, 3992 (1931).

whereas when approximately two volumes of nitrogen are present to one of hydrogen it has dropped to 1465°.

These results are of interest in showing the marked effect that inert gases such as nitrogen have on the maximum flame temperature of combustibles when burned with air and emphatically suggest the importance of keeping inerts in manufactured gas and other industrial gaseous fuels to a minimum if a maximum flame temeerature is desired.

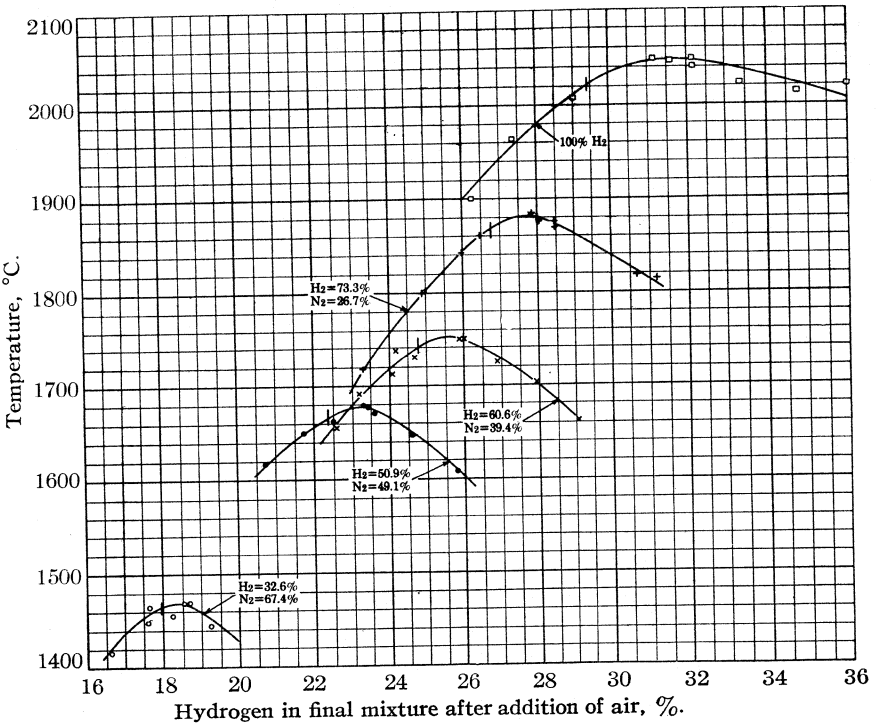


Fig. 1.—Flame temperatures H_2–N_2–air mixtures.

In the curves shown in Fig. 1, the percentages of hydrogen present representing complete combustion are indicated by short vertical lines crossing the curves. In agreement with results previously obtained for other combustibles,[5a,b,c] the maximum temperatures occur slightly on the rich side.

Figure 2 shows graphically the decrease in the maximum flame temperature with increase in nitrogen content. The decrease is almost directly proportional to the percentage of nitrogen in the original hydrogen–nitrogen mixture before the addition of air. It was found impossible to obtain flame temperatures, by the method used, when more than about two volumes of nitrogen was present for one volume of hydrogen, because

the reversal of the sodium line was too indistinct. Determinations with larger proportions of nitrogen were abandoned.

The Flame Temperatures of Ammonia–($3H_2 + N_2$)–Air Mixtures.—It was found impossible to burn straight ammonia in air (in order to obtain its flame temperature) at laboratory temperature with the various burners tried. The rate of flame propagation is too small to prevent the flame from blowing off the burner ports. Determinations were made with mixtures of ammonia and its dissociation products ($3H_2 + N_2$). An extrapolation for the maximum flame temperature of pure ammonia might then be made from these data.

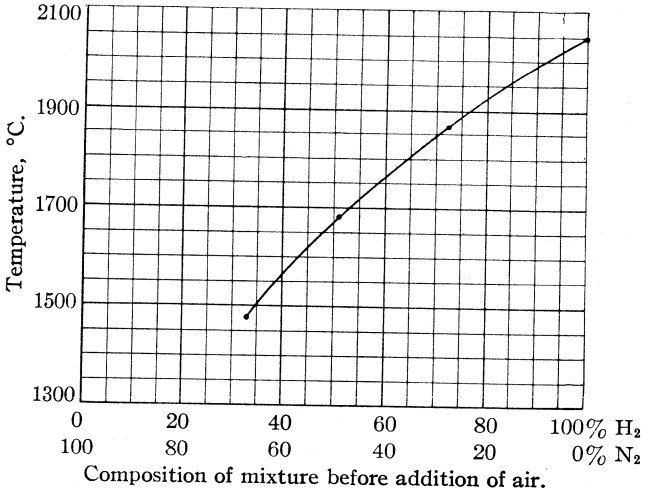


Fig. 2.—Maximum flame temperatures H_2–N_2–air mixtures, determined values.

Since ammonia is very soluble in water and glycerin–water mixtures the procedure for preparation of the gas mixtures had to be altered. They were prepared and stored in a high-pressure cylinder. Ammonia, nitrogen and hydrogen under high pressure (in tanks) were measured into an empty cylinder by means of a calibrated pressure gage in desired amounts. The gases were mixed by tilting the cylinder and applying gentle heat on one side near the bottom. Due to the convection currents set up, it was found that one hour was sufficient to mix the gases thoroughly. Samples of gas were then withdrawn for analysis. One sample was stored over dilute acid solution to absorb the ammonia. The unabsorbed gases, hydrogen and nitrogen were then transferred to a Bone and Wheeler gas analysis apparatus and determinations made for hydrogen, oxygen and nitrogen (the latter by difference). The percentage of oxygen present in the sample was assumed to be due to contamination by air. Correction for the amount of nitrogen associated with oxygen in air was made. If the ratio

of hydrogen to nitrogen was not three to one, more of one of the gases was added and the analysis repeated. For the analysis of ammonia the gas was passed into a 240-cc. calibrated sample tube and the sample taken over clean dry mercury. The temperature and pressure were recorded. The gas sample was passed through two efficient absorption bulbs (Bowen type) containing $N/10$ sulfuric acid. The unneutralized acid was titrated back with standard ammonium hydroxide solution using a cochineal indicator. The percentage of ammonia could then be calculated. Knowing the ammonia content the percentage of hydrogen and nitrogen in the original mixture could then be evaluated.

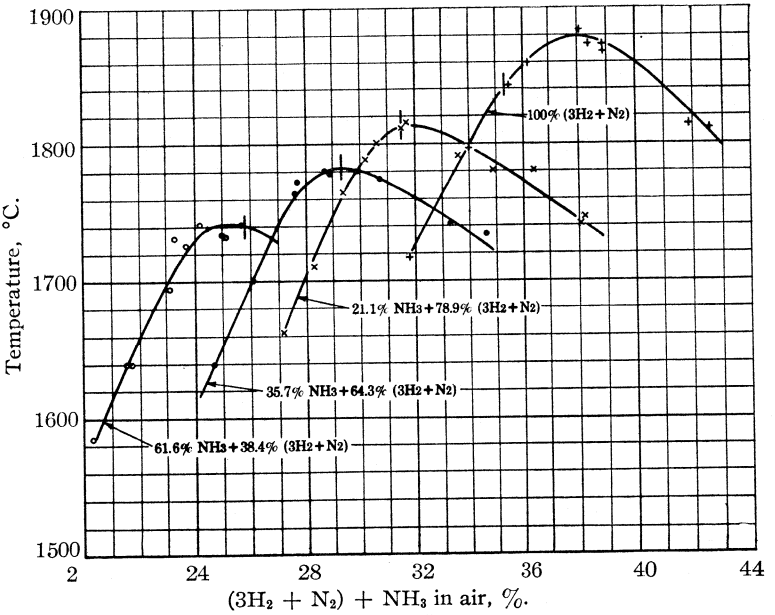


Fig. 3.—Flame temperature of mixtures of ammonia and its products of dissociation in air.

The flame temperatures of mixtures of ammonia and its dissociation products are shown in Fig. 3. The maximum flame temperature decreases with increasing proportions of ammonia. For 61.6% ammonia in the original combustible mixture it is 1740°. It was impossible to determine flame temperatures on the rich side of this mixture because the flames elongated and blew off the burner ports. Determinations for mixtures containing more than 61.6% ammonia were discontinued. The maximum flame temperatures occur slightly on the rich side except for the mixture containing the highest proportion of ammonia.

The maximum flame temperatures are plotted in Fig. 4. It is of interest to compare these with the maximum flame temperatures of the mixtures

calculated by the method described elsewhere[5b] and represented by the upper curve in Fig. 4. They are about 75° higher than the observed, which is attributable to radiation losses. This difference is constant over the range investigated. The calculated maximum flame temperature for ammonia–air mixtures is 1775°. On this basis, assuming the difference to hold throughout the entire range, the observed maximum flame temperature of ammonia–air mixtures, if a laboratory burner could be developed to burn them, would be about 1700°.

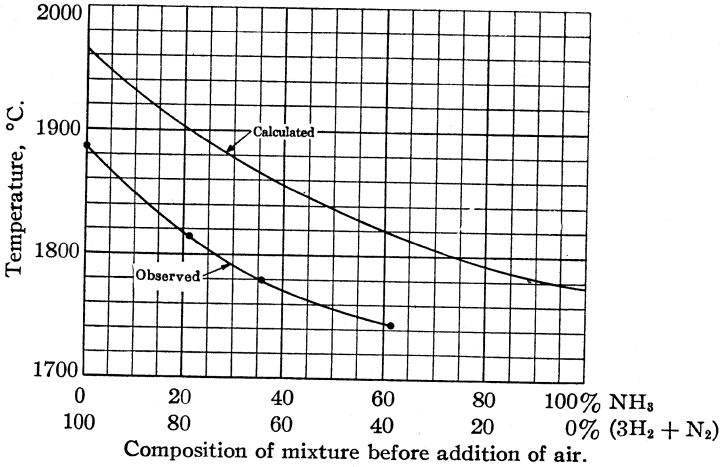


Fig. 4.—Maximum flame temperatures of ammonia–($3H_2 + N_2$)–air mixtures.

Summary

The flame temperatures of hydrogen–nitrogen–air mixtures and ammonia–($3H_2 + N_2$)–air mixtures have been measured by the sodium line reversal method.

The maximum flame temperature of a mixture $3H_2 + N_2$ is 1885°—about the same as that found for methane or Pittsburgh natural gas burning in air. Temperatures for other proportions of hydrogen and nitrogen are given.

The maximum flame temperature of ammonia, as determined by extrapolation, is 1700°.

The flame temperatures have been calculated and are in good agreement with the observed values.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 82 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

A THEORY FOR THE ACTIVITY OF CONTACT CATALYSTS

BY H. G. TANNER

RECEIVED NOVEMBER 4, 1931 PUBLISHED JUNE 6, 1932

During a study of the reaction of hydrogen and oxygen at low pressures on platinum wires[1] the observation was made that the activity of the wire was a function of the difference in temperature between the wire and the wall of the reaction tube. The pressure was such that the mean free path of the molecules was greater than the distance from the wire filament to the wall of the tube. If the wire and tube were at the same temperature the reaction would not proceed. When the wire was heated 50 to 100° higher than the temperature of the wall a reaction occurred. This was true for wall temperatures ranging from −180 to +200°. If a reaction was progressing, its speed would be increased merely by cooling the wall, and retarded if the wall temperature was made to approach the wire temperature. Appropriate experiments proved that this peculiar effect was not due to gas concentration, nor to the rate at which water vapor was removed from the reaction tube. The vessel wall had no catalytic effect since it made no difference whether the wall was Pyrex, fused silica, aluminum or molybdenum oxide-coated Pyrex. There was no alternative to the conclusion that the reaction rate was a function of the dissipation of energy from the catalyst wire, or, in other words, of the difference in temperature between the catalyst wire and the vessel wall. This conclusion led to a modified concept of catalytic activity.

Accurate measurements of the amounts of energy supplied to the wire were made as follows.

A small resistance of 0.30 ohm was connected in series with the catalyst. The construction of this resistance was such that its temperature would not depart appreciably from room temperature during the course of the experiment. A Leeds and Northrup thermocouple potentiometer was connected across this resistance as shown in Fig. 1. This arrangement furnished a precision null method by which the current through the catalyst arm of the Wheatstone bridge could be determined without disturbing the Wheatstone bridge balance.

As an example of the data obtained the voltage across the auxiliary resistance was found in a typical experiment to be 19.4 millivolts when the bulb of the catalyst tube was at 23°. The current flowing through this arm of the Wheatstone bridge was therefore 0.0647 ampere. Since the resistance of the catalyst filament was at that time 9.00 ohms (correspond-

[1] H. G. Tanner and G. B. Taylor, THIS JOURNAL, 53, 1292 (1931).

ing to 100°), the power supplied to the filament was 0.0377 watt. When liquid air was placed around the bulb the current through the catalyst arm of the Wheatstone bridge had to be increased to 0.138 amp. in order to maintain the catalyst resistance (average temperature) constant at 9.00 ohms. The power, therefore, was 0.171 watt. The ratio of these two wattages is as 1 is to 4.5. This means that four and a half times as much energy was being dissipated from the wire when the bulb was at −180° as when the bulb was at room temperature.

The ratio of the energies dissipated with bulb at room temperature and at liquid air temperature varied not only with the gas pressure, the nature of the gas and other obvious factors, but also with the condition of the wire surface. The higher the catalytic activity of the wire the greater the effect of the bulb temperature upon the rate of reaction, and upon the abnormal cooling of the filament. These observations show that an intimate connection exists between thermal accommodation coefficient and catalytic activity and indicate that the accommodation coefficient itself may be a function of temperature difference.

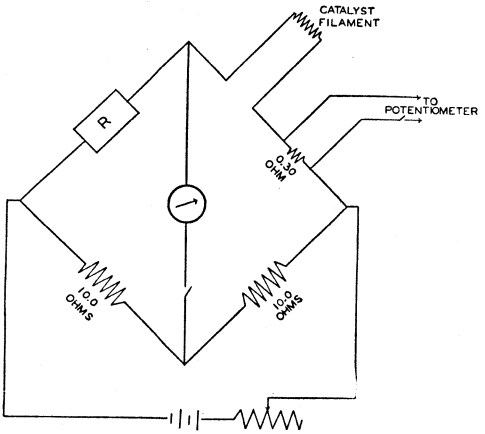


Fig. 1.—Diagram of electrical connections.

It may be mentioned that the peculiar effect of bulb temperature upon the heat transfer from the wire was proved to depend upon the gases present and not upon the filament end-losses, or radiation. When the bulb was exhausted to a pressure below 1×10^{-6} mm., the heat losses from the filament were practically independent of the bulb temperature.

Speculations about catalytic activity frequently have been concerned rather with the mechanism of catalytic activation than catalytic activity in the strict sense of the term. Catalytic activity is an expression of the efficiency of a catalyst, and it should always be distinguished from the mechanism of catalytic activation. Concepts such as "elementary spaces," "stretched molecules," etc., assist in giving a definite picture of the way in which adsorption may occur, and how certain areas on a catalytic surface activate molecules, but these concepts are not sufficient to account for the difference in activity of two or more catalysts which may be chemically identical. This difference in activity has always been regarded as due to a difference in the number of active spots exposed. There is another possibility, however, which is worthy of consideration, *e. g.*, the rate

at which the active spots function. The efficiency of the active spots rather than their number may be the controlling factor.

The mechanism of adsorption plays a prominent part in current theories of catalysis. Although adsorption undoubtedly is of great importance, yet a catalyst functions only when molecules get up to the active spots, react, and the reaction products depart. Adsorption is but a part of this process. In a sense, a catalyst (more accurately the active spots) must "breathe" in order to function. Current theories stress adsorption, but give little or no consideration to the "exhalation" part of the cycle. The complete cycle of "respiration" and the rate of its occurrence are fully as important as the mechanism of adsorption.

The respiratory action is explained in this paper by assuming that the active spots fluctuate in temperature. During moments when one of them is below the average temperature, adsorption occurs. A little later this spot becomes hot (from Brownian motion of adjacent molecules, or chemical reaction, etc.), and the adsorbed molecule departs as a different chemical entity. When the spot has cooled the process repeats. From this viewpoint, catalytic activity is governed by those forces which control the temperature fluctuations of the active spots.

In the experiments above described no reaction occurred, for example, when the wire and wall were both at 100°. Maxwell's law of temperature probability could be applied to any given atom on the wire surface because a condition of thermal equilibrium existed. The probability that an atom departed a hundred degrees, say, from the average temperature was very small. Maxwell's law cannot be applied, however, when thermal equilibrium does not exist. It is not applicable to "steady state" conditions. When, in the experiment, the bulb was cooled by liquid air, gas molecules at −180° struck the filament whose average temperature was maintained at 100°. The probability that a given atom on the filament would be at 0°, for instance, was very much increased. The average temperature of the filament, however, was forcibly maintained at 100°. Therefore the probability of a given atom on the filament having a temperature of 200°, say, was greatly increased, as compared to thermal equilibrium conditions. In other words, for a given degree of probability, an atom on the wire surface fluctuated through a wider temperature range. The "time-lag" of gas molecules striking the filament was increased by their having a lower temperature at the moment of collision, and the probability of their subsequent activation, reaction and desorption was increased by their attainment of the postulated abnormally high temperatures. The rate of "respiration" of the active spots was increased because their fluctuations in temperature were either extended, or, for a given temperature change, made more rapid. The increased reaction rate which accompanied the temperature difference in the experiments described above is therefore explained.

The rate of clean-up of certain pure gases by hot filaments was found by I. Langmuir[2] to be increased when the temperature of the bulb was lowered. Nitrogen, for example, was cleaned up by a hot molybdenum filament very rapidly when the bulb was cold. Langmuir's explanation for the bulb-temperature effect was built upon the assumption that the rate of evaporation of the molybdenum was independent of the bulb temperature. The increased rate of clean-up was attributed to a higher reaction efficiency per collision of molybdenum vapor molecules and nitrogen when the bulb temperature was low.

An alternative explanation can be offered from the viewpoint of the hypothesis developed in this paper by assuming that the rate of evaporation of molybdenum was the controlling factor involved, and that this rate was affected by the temperature of the bulb. When a cold molecule of nitrogen struck the filament, a cooling effect occurred at that point. Since the average temperature of the filament was kept constant, an adjacent atom of molybdenum must therefore have acquired an abnormally high temperature. Since the rate of evaporation of molybdenum was shown by Langmuir to be an exponential function of temperature with a high coefficient, the greatly increased rate of evaporation from the abnormally high temperature areas would produce a net increase in the gross rate of evaporation. The greater amount of molybdenum vapor produced would of course account for the increased rate of reaction with nitrogen. If this interpretation be accepted there appears to be no fundamental difference in the effect of bulb temperature in these clean-up experiments, and in the catalytic experiments just described. Conversely, the fact that two independent examples of the bulb-temperature effect can be explained on a common basis lends support to the theory.

In the ordinary use of a catalyst the abnormal temperature fluctuations of the active spots are probably set up by any condition capable of disturbing thermal equilibrium. Adsorption desorption, and chemical reaction, for example, are processes involving large heat changes. Each of these processes would greatly disturb the normal Maxwellian variation of temperature of an active spot. An active spot may momentarily attain a temperature many degrees, perhaps many hundred degrees in case of gases, above or below the average temperature. Even when a liquid surrounds a catalyst, as for example an oil around nickel-on-kieselguhr, Armstrong and Hilditch[3] found evidence that some of the nickel particles during hydrogenation must have attained a temperature above 300°, although the oil appeared always to be below 180°. This is significant, because it means that the particles of nickel fluctuated in temperature between these limits at least.

[2] Langmuir, THIS JOURNAL, **41**, 167 (1919).

[3] Armstrong and Hilditch, *Proc. Roy. Soc.* (London), **A108**, 111 (1925).

If the foregoing postulates concerning the temperature variation of active spots and catalytic activity be granted, other catalytic phenomena can be explained with the help of a few minor postulates. The beneficial effect of a rough surface, for example, is easily explained provided one grants that temperature oscillations are greater for an active spot located on a spire of a rough surface compared to the temperature variations of an active spot on a smooth surface. This assumption is not unreasonable because an atom located on the tip of a microscopic spire has less chance to stay in thermal equilibrium with its surroundings than an atom lying on a smooth surface.

The difficulty of correlating catalytic activity with adsorption can likewise be explained. Porous substances are good adsorbents. Some of them are good catalysts. Adsorption, however, is unidirectional and not "respiratory" or cyclic in character. Furthermore, adsorption probably occurs to a major extent *within* the capillary spaces of a porous substance, whereas catalysis is postulated to occur *on* the surface, *e. g.*, on the projecting spires at the mouths of the capillaries. A porous material may be one having capillaries highly branched within the body of the substance, or it may have a capillary structure such that most of the capillaries are short, and terminate on the external surface. The former would not be as rough a surface as the latter, but would probably adsorb a greater quantity of material. Porosity and roughness are therefore related. Similarly, adsorption and catalytic activity are related, but the relationship in either case will always evade any general quantitative treatment.

There is nothing in this explanation which would preclude some catalysis occurring in the depths of the capillaries of a porous substance, but in view of the respiratory nature of catalysis, and the slow rate of diffusion into and out of tiny capillaries, the interior surface of any capillary less than 1000 Å. in diameter probably plays but a minor role.

Catalyst supports must profoundly influence the temperature variations of the catalyst particles distributed thereon. When nickel oxide is precipitated on kieselguhr, for example, and subsequently reduced, the nickel does not form a continuous surface. The catalyst support protrudes here and there all over the surface. Ultramicroscopic specks of nickel are "imbedded" in a thermally different material. This heterogeneity of the surface is favorable to large temperature fluctuations of the nickel specks. A reaction occurs on a speck of nickel, thereupon the temperature is raised perhaps a hundred degrees or more.[3] If this heat be not dissipated too rapidly, desorption occurs. Later the speck cools so that adsorption and reaction can again occur. Were it not for the thermal insulating effect of the catalyst support, the nickel speck could not attain as high a momentary temperature. A spot on massive smooth nickel would, in comparison, stay nearly constant in temperature because of the easier exchange of energy with neighboring atoms.

Promoters which do not act chemically may function by increasing the physical heterogeneity of the surface, and thereby accentuate the local temperature fluctuations. Clean liquid surfaces rarely, if ever, function as heterogeneous catalysts. The reason for this may well be that the active spots (elementary spaces) maintain a relatively uniform temperature.

Electron emission from heated filaments varies exponentially with temperature, and is always observed under thermal conditions far removed from equilibrium. Therefore, the concept of abnormal surface temperatures developed above may find application in explaining some of the peculiarities of electron emission. Roughness of surface, the rate of heat transfer from core metal to oxide coating, and a heterogeneous ("promoted") surface may each be factors to be considered. A study of the flicker effect[4] with variation in the temperature of the gas striking the filament might yield information of value in substantiating or refuting the above developed theory, especially if K. H. Kingdon's[5] suggestion that the flicker effect involves surface temperature fluctuations is found to be true.

Summary

Catalytic activity is postulated to depend upon the rate at which active spots function.

The action of an active spot is regarded as respiratory in character, and dependent upon fluctuations in temperature of these spots.

The concept of "average temperature" is discussed, and the probable thermal behavior of rough, heterogeneous surfaces is contrasted with that of smooth, homogeneous surfaces.

These concepts afford a partial explanation of variations in catalytic activity occasioned by promoters, supports, roughness of surface, porosity, etc.

The suggestion is made that electron emission may be influenced by the same thermal conditions which affect catalytic activity.

WILMINGTON, DELAWARE

[4] G. B. Johnson, *Phys. Rev.*, **26**, 71 (1925); W. Schottky, *ibid.*, **28**, 74 (1926); I. Langmuir and K. H. Kingdon, *ibid.*, **34**, 129 (1929).

[5] Kingdon, *ibid.*, **37**, 89 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

THE RATE OF DECOMPOSITION OF XANTHIC ACID

BY CECIL V. KING AND EMILIE DUBLON

RECEIVED DECEMBER 19, 1931 PUBLISHED JUNE 6, 1932

Introduction

It was suggested by Brönsted in 1925 that a study of the kinetics of the decomposition of the xanthic acids in aqueous solution would be valuable, and preliminary experiments were carried out by one of the present writers (C. V. K.). These experiments were discontinued because no convenient method was available for measuring the rates accurately.

The methyl and ethylxanthic acids are neither as strong as hydrochloric nor as weak as the ordinary organic acids, but are somewhat stronger than dichloroacetic acid. Both primary and secondary salt effects influence their decomposition rates, in the acid solution alone and in buffer solutions. Accurate measurements of the rates were made and the results were analyzed by v. Halban and his co-workers before the development of salt effect theory; consequently the importance of both types of salt effect was neglected entirely.

The rate of decomposition was first studied in detail by v. Halban and Kirsch,[1] who prepared the free methyl and ethylxanthic acids, found a method of stabilizing them, and studied their decomposition in a number of solvents. Roughly, the rate increases with the polarity of the solvent; in solvents of low dielectric constant it is autocatalytic because of the alcohol formed, but this is not true in alcohol itself or in water.

V. Halban and Hecht[2] published the results of an extensive study of the rates in aqueous solution. Potassium ethyl or methyl xanthate solutions were mixed with hydrochloric acid in known concentrations and the solutions analyzed at suitable time intervals; although the reaction was very rapid, the measurements were carried out with such precision, over such a wide concentration range and to such low ionic strengths that in some respects they are ideal for reinterpretation on the basis of the newer theories.

It was assumed that the reaction was a unimolecular decomposition of undissociated xanthic acid, although v. Halban recognized that this is kinetically identical with a bimolecular reaction between the hydrogen and xanthate ions. The unimolecular "k" increases and reaches a maximum value as the hydrochloric acid concentration is increased; from the ratio of the rate constants the dissociation constants were calculated. The values obtained were 0.030 for ethylxanthic acid, 0.034 for methylxanthic

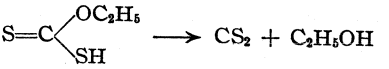
[1] V. Halban and Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).

[2] V. Halban and Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

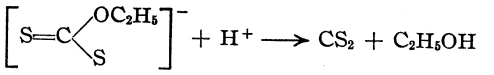
acid; we shall show later that these are correct for zero ionic strength but not for finite salt concentrations.

Experimental

Our own experiments were carried out with ethylxanthic acid in acetic acid–sodium acetate and aniline-aniline hydrochloride buffers. Since the xanthic acid is so strong, no appreciable amount of undissociated acid will remain in these buffers, and salt effect on this equilibrium can be neglected. The reaction may take place by either of the following mechanisms



or



but since the concentration of undissociated xanthic acid is controlled by the xanthate and hydrogen-ion concentrations, these lead to the same kinetic equation

$$\frac{dx}{dt} = kC_{H^+}C_{X^-}\frac{f_1^2}{f_0} \qquad (1)$$

where X^- is used for the xanthate ion, f_1 and f_0 are activity coefficients of the univalent ions and neutral reaction complex.

Since the hydrogen-ion concentration of an acetic acid–acetate buffer is given by

$$C_{H^+} = K_{0,\,HAc}\frac{C_{HAc}f_0}{C_{Ac^-}f_1^2}$$

the final rate equation in such a buffer becomes with close approximation

$$k = \frac{2.3}{Kt}\left[\frac{a+c}{b-a}\log\frac{a}{a-x} - \frac{b+c}{b-a}\log\frac{b}{b-x}\right] \qquad (2)$$

where a is initial xanthate concentration, b is initial acetic acid concentration, c is initial acetate-ion concentration; this is formally identical with the classical rate expression where salt effects are neglected.

In the aniline–anilinium ion buffer, however

$$C_{H^+} = K_{0,\,AnH^+}\frac{C_{AnH^+}}{C_{An}}\frac{1}{f_0}$$

and when this is substituted in (1) the activity coefficients do not cancel. Consequently, when the classical expression (2) is used for calculating the rates in these buffers, we shall expect that as the ionic strength is increased, the values of k will diminish in accordance with the relation[3]

$$k = k_0\frac{f_1^2}{f_0^2}$$

[3] See Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924), for a discussion of salt effects in these buffers.

Potassium xanthate was recrystallized from aqueous alcohol until the fresh solution was neutral to phenolphthalein; the crystals were sucked dry and further dried over sulfuric acid. Standard acetic acid was partially neutralized to prepare buffers. Aniline was distilled three times and weighed amounts dissolved in standard hydrochloric acid for stock solutions.

The reactions were followed by measuring the increase in vapor pressure above the solutions, chiefly due to the carbon disulfide formed, in a modification of the apparatus designed by Brönsted.[4] After introducing 100 cc. of the buffer solution into the reaction flask, a weighed amount of potassium xanthate in a glass capsule was suspended from a hook in the neck, the neck was sealed off and the entire apparatus was evacuated (while shaking) and sealed. When the pressure reading became constant the xanthate was dropped in and quickly dissolved, and pressure readings taken at frequent intervals. The thermostat was kept at 25 ± 0.02°.

Several pressure readings which fell on a smooth curve through all readings were selected to calculate the rate constants. These can be calculated from equation (2) by using pressure readings directly or by calculating and using actual concentrations.

Acetic Acid–Acetate Buffers.—Details of a typical experiment are given in Table I.

TABLE I

INITIAL CONCENTRATIONS: $C_{KX} = 0.015M$, $C_{HAc} = 0.04M$, $C_{NaAc} = 0.01M$

t, min.	x (m. p. l.)	k[a]
20	0.00401	253
40	.00625	267
60	.00778	268
92	.00951	270
116	.01048	274
152	.01144	270
		Average 267, av. dev., 4.7

[a] $K_{0,\ HAc} = 1.86 \times 10^{-5}$.

Table II summarizes a number of experiments in which the hydrogen-ion concentration was kept approximately the same at the beginning of each experiment, and shows that there is no unusual effect of the undissociated acetic acid. Table III summarizes experiments in which the initial hydrogen-ion concentration was varied, and shows that the values of k are independent of this factor (which is also indicated by the constancy of k in individual experiments, since C_{H^+} decreases considerably during the reaction with the buffer concentrations used). Table IV shows that k is not affected by changing the initial xanthate concentration, although the limitations of the apparatus used made it impossible to vary this over a wide range.

[4] King, THIS JOURNAL, **50**, 2090 (1928).

TABLE II

Initial concentrations			
C_{KX}, M	C_{HAc}	C_{NaAc}	k
0.015	0.04	0.01	271
.015	.05	.0125	255
.015	.05	.0125	266
.015	.10	.025	284
.015	.10	.025	266
.015	.10	.025	279
.015	.10	.025	278
.015	.20	.05	279
.015	.20	.05	262
			Av. 271, av. dev., 8

TABLE III

Initial concentrations			
C_{KX}	C_{HAc}	C_{NaAc}	k
0.015	0.05	0.025	278
.015	.05	.025	278
.015	.075	.025	266
.015	.10	.025	278[a]
.015	.125	.025	262
.015	.15	.025	267
			Av. 273, av. dev., 7

[a] Average of four experiments.

TABLE IV

C_{KX}	C_{HAc}	C_{NaAc}	k
0.015	0.075	0.025	266
.01	.075	.025	270
.01	.075	.025	275
			Av. 270

At higher salt concentrations the activity coefficients do not cancel and equation (2) is no longer valid; this is shown in Table V where the marked diminution of k is evident when sufficient inert salt is added.

TABLE V

C_{KX}	C_{HAc}	C_{NaAc}	C_{KCl}	k
0.015	0.04	0.01	0	271
.015	.10	.025	.2	250
.010	.10	.025	.4	252
.010	.10	.025	.4	260
.015	.04	.01	.5	250
.015	.10	.025	.75	235
.015	.10	.025	1.0	221

Aniline–Anilinium Ion Buffers.—Since the dissociation constant of the anilinium ion is near that of acetic acid[5] these mixtures give a suitable

[5] See Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

hydrogen-ion concentration. The value of K_{AnH^+} used in calculating the constants in Tables VI and VII may be several per cent. in error for 25°, but not enough to obscure the results. Since the ionic strength decreases during the reaction, and the buffer equilibrium has no positive salt effect to neutralize the negative effect on the reaction, the values of k should increase during each experiment. Actually the decrease in ionic strength was not sufficient in any of our experiments to make this evident. Details of typical experiments are given in Table VI.

TABLE VI

Initial concentrations $C_{KX} = 0.015\ M$, $C_{AnH^+} = 0.114\ M$, $C_{An} = 0.036\ M$			Initial concentrations $C_{KX} = 0.015\ M$, $C_{AnH^+} = 0.0855\ M$, $C_{An} = 0.0195\ M$		
t	x	k[a]	t	x	k[a]
20	0.00345	199	20	0.00430	201
32	.00495	196	32	.00596	198
40	.00578	195	40	.00688	198
56	.00706	187	56	.00840	200
80	.00890	192	80	.01000	200
112	.01060	196	112	.01148	200
176	.01260	198	176	.01322	205
		Av. 195			Av. 200

[a] $K_{AnH^+} = 2.2 \times 10^{-5}$.

Table VII summarizes several experiments in which the hydrogen-ion concentration and the ionic strength were varied. It is evident that only the change in ionic strength affects the value of k. At the ionic strength 0.094, $k = 200$, much lower than the average value $k_0 = 271$ obtained from the acetic acid buffers. The sign and magnitude of the salt effect agree well with the predicted.

TABLE VII

C_{KX}	C_{AnH^+}	C_{An}	C_{NaCl}	μ(mean)	k
0.015	0.0855	0.0195	0	0.0939	200
.015	.114	.036		.122	195
.015	.114	.027		.122	192
.015	.114	.019		.122	184
.015	.114	.027	.2	.322	155
.015	.114	.036	.5	.622	129
.015	.0855	.0195	1.0	1.094	105

Analysis of the Data of v. Halban and Hecht.—The measurement of v. Halban and Hecht were all made at 0°, mostly in such dilute solutions that the change in ionic strength during each reaction was considerable. When k is calculated from the classical bimolecular expression

$$\frac{dx}{dt} = kC_{H^+}C_{X^-}$$

the changing salt effect causes the values of k to increase during each experiment, as is shown in Table VIII.

TABLE VIII

INITIAL $C_{KX} = a$, INITIAL $C_{HCl} = b$, TEMPERATURE, 0°

t, min.	v. Halban's Table 2 $a - x$	$b - x$	k		v. Halban's Table 4 $a - x$	$b - x$	k
0	0.0144	0.0185	..	0	0.00846	0.01006	..
2.5	.01122	.0153	5.80	13	.00359	.00519	9.38
4	.00956	.0137	6.66	15	.00319	.00479	9.70
5	.00854	.0126	6.75	20	.00242	.00402	10.44
8	.00661	.0107	7.01				

Because of the complication of undissociated acid formation it is impossible in this case to apply the method outlined by Scatchard for reactions in a changing environment.[6] We have tabulated the initial values of k (bimolecular) for v. Halban's measurements on ethylxanthic acid, and

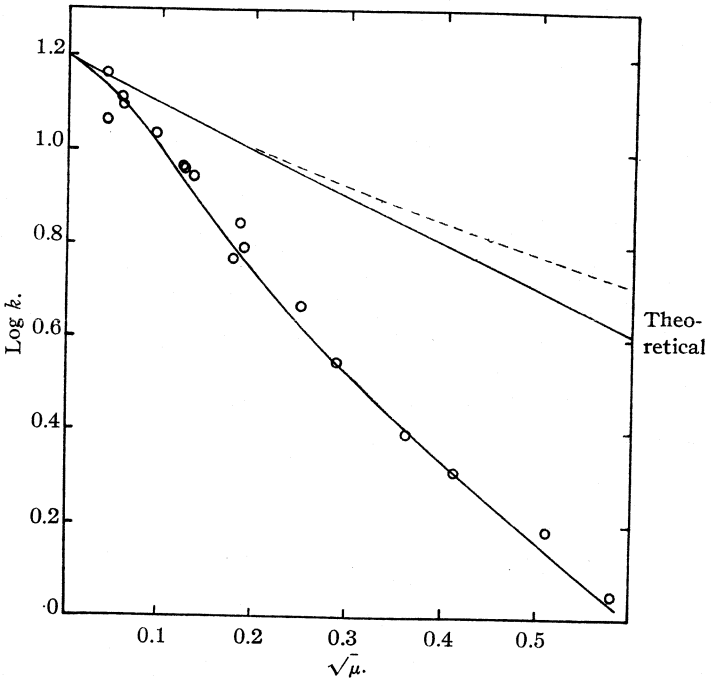


Fig. 1.—Comparison of observed rates with the theoretical for ethylxanthic acid at 0°: theoretical slope, − 0.97.

also the mean values of the ionic strength during each initial measurement (Table IX). In Fig. 1 the values of log k are plotted against $\sqrt{\mu}$. If we could use the correct ion concentrations to calculate k, the experimental points should approach the theoretical relation

$$\log k = \log k_0 - 0.97 \sqrt{\mu} \text{ (at 0°)}$$

[6] Scatchard, THIS JOURNAL, **52**, 52 (1930).

as the ionic strength decreases, and deviations from this should be positive rather than negative, as indicated by the dotted line of Fig. 1. On the other hand, the change in dissociation constant with ionic strength at low concentrations is given by

$$\log K = \log K_0 + 0.97\sqrt{\mu} \qquad (3)$$

and deviations from this with increasing ionic strength will be negative. These two relations can now be used to evaluate K.

TABLE IX

BIMOLECULAR "CONSTANTS" FOR ETHYLXANTHIC ACID AT 0°

v. Halban's table	$\sqrt{\mu}$	k	v. Halban's table	$\sqrt{\mu}$	k
9	0.0409	14.55[a]	1	0.185	7.03
9	.0434	11.54	39	.190	6.21
8	.0570	12.99	37	.251	4.67
7	.0605	12.59	31	.290	3.50
6	.0953	10.86	38	.364	2.46
4	.126	9.38	35	.41	2.07
5	.127	9.20	40	.51	1.52
3	.136	8.76	36	.58	1.14
2	.177	5.80	32	.71	0.77

[a] "Interval constant" from the last two measurements.

For equal concentrations of H^+ and X^-, the k we have calculated is given by

$$k = \frac{1}{at}\frac{x}{(a-x)}$$

But if m is the average concentration of undissociated xanthic acid during the measurement, the rate is more correctly given by

$$k_w = \frac{1}{(a-m)t}\frac{x}{(a-m-x)}$$

and as $x \doteq 0$

$$\frac{k_w}{k} = \frac{a^2}{(a-m)^2}$$

Since $2a - m = \mu$, this gives finally

$$m = \mu\frac{\sqrt{k_w/k} - 1}{\sqrt{k_w/k} + 1} \qquad (4)$$

The dissociation constant can be expressed by

$$K = \frac{(\mu - m)^2}{4m} \qquad (5)$$

and substituting (4) in (5) gives

$$K = \frac{\mu}{k_w/k - 1} \qquad (6)$$

By a series of trials, equation (6) was used to draw the curve shown in Fig. 1 through the experimental points. The values of k_w/k used are given in Table X, and Fig. 2 shows that these values make equation (3)

TABLE X

$\sqrt{\mu}$	k_w/k	K
0.05	1.071	0.035
.1	1.26	.038
.2	1.82	.049
.3	2.40	.064
.4	3.02	.079
.5	3.63	.095

The values of K above $\sqrt{\mu} = 0.2$ are actually too high, but are used in extrapolating to $\mu = 0$.

valid. The extrapolated value for K_0 becomes 0.031, in good agreement with v. Halban's value 0.030. The dotted line in Fig. 2, rather than the solid line, shows the expected course of K with increasing ionic strength; no change in K appears with v. Halban's method of calculation.

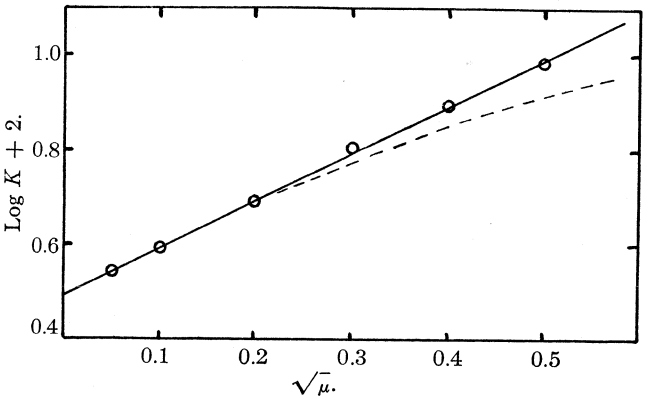


Fig. 2.—Variation in dissociation constant of ethylxanthic acid with ionic strength (see Table X): theoretical slope, +0.97.

Tables XI and XII, Figs. 3 and 4, show the same treatment applied to the measurements on methylxanthic acid. The extrapolated value of K_0

TABLE XI

BIMOLECULAR "CONSTANTS" FOR METHYLXANTHIC ACID AT 0°

v. Halban's table	$\sqrt{\mu}$	k	v. Halban's table	$\sqrt{\mu}$	k
16	0.0472	14.03	19	0.251	5.30
14	.0933	12.41	17	.359	3.05
15	.0933	11.89	20	.365	3.13
13	.135	8.95	25	.373	3.06
12	.143	9.61	17	.503	1.65
18	.182	7.47	21	.507	1.71
11	.190	7.54	26	.514	1.88
11	.193	6.40	17	.710	0.82
24	.200	7.10	22	.712	.91
10	.244	6.32	27	.717	.93

TABLE XII

$\sqrt{\mu}$	k_w/k	K
0.05	1.064	0.039
.1	1.230	.0435
.2	1.73	.055
.3	2.28	.070
.4	2.83	.087
.5	3.85	.106

The values of K above $\sqrt{\mu} = 0.2$ are actually too high, but are used in extrapolating to $\mu = 0$.

is 0.035, again in good agreement with the "average" of v. Halban. The broken lines again show the type of deviations from the theoretical to be expected for log k and log K. We estimate that these values of K_0 cannot be in error by more than $\pm 5\%$.

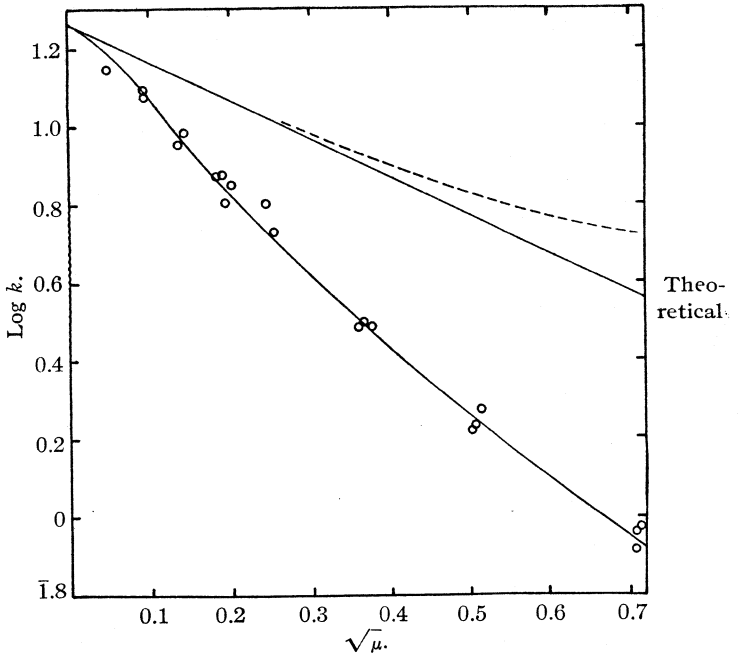


Fig. 3.—Comparison of the observed rates with the theoretical for methylxanthic acid at 0°: theoretical slope, −0.97.

The Temperature Coefficient.—It is perhaps inaccurate to calculate the temperature coefficient from the data of v. Halban and Hecht at 0° and ours at 25°, since the rates were measured by different methods and at far different hydrogen-ion concentrations. However, the coefficient is certainly unusually high, as is to be expected from the rapidly decreasing stability of solutions of the acids and their salts as the temperature rises.

Using k_0 for ethylxanthic acid as 16.0 at 0° (Fig. 1) and 270 at 25°, we obtain an average coefficient per 10° rise of 6.75.

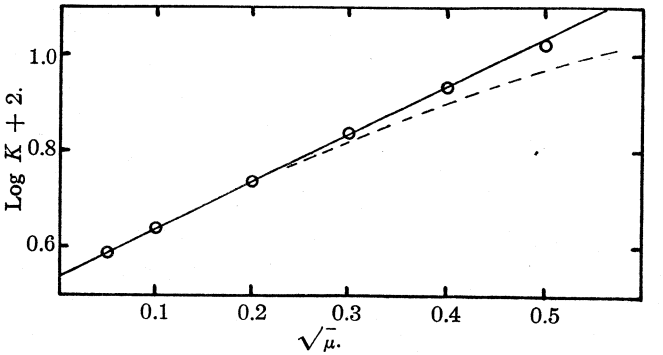


Fig. 4.—Variation in dissociation constant of methylxanthic acid with ionic strength (see Table XII): theoretical slope, +0.97.

Summary

Measurements of the rate of decomposition of ethylxanthic acid have been made at 25° in acetic acid–acetate and aniline–anilinium ion buffers and the primary and secondary salt effects analyzed.

Previous measurements of the rates for ethyl and methylxanthic acids have been analyzed and shown to be complicated by salt effects. The influence of salts on the dissociation constants of these acids has been shown.

The temperature coefficient of the rate has been calculated and shown to be unusually high.

NEW YORK CITY

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 91]

THE DISSOCIATION PRESSURE OF SILVER OXIDE BELOW 200°

BY ARTHUR F. BENTON AND LEONARD C. DRAKE

RECEIVED DECEMBER 21, 1931 PUBLISHED JUNE 6, 1932

Introduction

Le Chatelier[1] first showed that the reaction $Ag_2O = 2Ag + {}^1/_2O_2$ is reversible. Careful measurements of the equilibrium pressure were subsequently made by Lewis[2] over the temperature range 302–445°, and by Keyes and Hara[3] from 374 to 500°. Close agreement was shown between the results of these two investigations.

Aside from the considerable interest which attaches to this system

[1] Le Chatelier, *Z. physik. Chem.*, **1**, 516 (1887).

[2] Lewis, THIS JOURNAL, **28**, 139 (1906).

[3] Keyes and Hara, *ibid.*, **44**, 479 (1922).

per se, it represents an essential step in one of the available methods[4] of calculating the thermodynamically important value of the free energy of formation of water at 25°. For this purpose, however, it is necessary to extrapolate the observations over a range of temperature of about 300°, without adequate specific heat data to serve as a guide. In addition a correction must be made because of the fact that at the high pressures obtaining in the measurements of Lewis and of Keyes and Hara (20 to 390 atm.), the fugacity of oxygen differs markedly from its pressure, and the thermodynamic activity of the solid phases is also affected. For these reasons a determination of the silver oxide equilibrium at lower temperatures has appeared desirable.

In the present work it has been found that even at temperatures as low as 160–170°, finely divided silver slowly takes up oxygen in indefinitely large quantities, and the pressure finally reached after each addition of gas is *independent of the amount already taken up*. Similarly, when gas is withdrawn from the system the pressure gradually builds up and finally approaches the same value as before. From an extensive series of such measurements the dissociation pressure of the oxide has been determined at five temperatures over the range 173–191°. From these results new values have been calculated for the free energy of formation of silver oxide, and for the free energy of formation of water at 25°.

Apparatus and Procedure

The apparatus was of the type recently used in this Laboratory for studies on gaseous sorption, and has been described by Benton and White.[5] Its essential parts are a bulb containing the solid under investigation, a mercury manometer to indicate the pressure in the bulb, a mercury-filled buret to measure the quantities of gas admitted or withdrawn, and a Töpler pump. The only difference between this new apparatus and the one previously described was the presence of a stopcock between the bulb and the remainder of the apparatus. This stopcock, the key of which was mercury-sealed at both ends, was the only one in the parts of the line communicating with the bulb, mercury seals being used elsewhere. The volume of the "free space" in the bulb and connecting capillary amounted to about 32 cc.

The buld was maintained at the desired temperatures by means of an electrically heated vapor-bath, lagged with asbestos paper, in which ethylene glycol was boiled under reduced pressure. The pressure in this bath was accurately controlled by means of a regulator similar to that described by Smith.[6] Fluctuations in temperature did not exceed 0.05°, even over the long periods of observation which were found necessary. The temperatures were measured with a mercury thermometer graduated to 0.2°, which was carefully standardized by reference to a similar thermometer newly calibrated by the U. S. Bureau of Standards. The necessary corrections for the exposed thread of mercury were applied.

Materials.—Metallic silver was prepared as follows. A solution of the calculated amount of barium hydroxide was added to an 8% solution of twice recrystallized silver

[4] Lewis and Randall, "Thermodynamics," 1923, p. 479.

[5] Benton and White, THIS JOURNAL, **52**, 2325 (1930).

[6] Smith, *Ind. Eng. Chem.*, **16**, 22 (1924).

nitrate at 80°. The precipitate was washed with conductivity water until no trace of barium could be detected, and then with ten liters of conductivity water in one-liter portions. It was then dried in air for twelve hours at 50°, and in oxygen for twenty-four hours at 100°. The oxide was reduced with purified electrolytic hydrogen, first for thirty hours at 30° and then for one hundred and fifty-three hours at temperatures gradually increasing to 100°. To avoid subsequent changes in the activity of the sample, it was finally heated for four hours at 150° and for ten hours at 300°. The mass employed was 39.4 grams.

Oxygen was generated by electrolysis of C. P. sodium hydroxide solution between nickel electrodes. It was purified by successive passage over heated platinized asbestos, calcium chloride, soda lime and phosphorus pentoxide.

Procedure.—After the bulb containing the sample was sealed to the apparatus, the silver was again reduced for an hour or two at 250°, and then subjected to thorough evacuation at this temperature. The bulb was then brought to 173.0° and oxygen was admitted in successive small portions. After each addition, to a pressure of approximately one atmosphere, the pressure dropped rapidly at first and then more slowly, finally tending toward a constant value after many hours. This procedure was repeated until a total of about 190 cc. of oxygen had been taken up, equivalent to the conversion of 9.3% of the silver to silver oxide. In these measurements the times of observation were not long enough to give more than an upper limit to the true equilibrium pressure. For the final measurements of dissociation pressures, the system which had been partially oxidized to the extent just described, was treated with a further portion of oxygen at about atmospheric pressure, and the decrease in pressure as a function of time was followed until equilibrium had apparently been reached. A constant value was usually obtained in five or six days. Similar measurements were then carried out at successively higher temperatures, equilibrium being approached in each case from the side of higher pressures. The bulb was then thoroughly evacuated at room temperature, and heated to 173°. The approach to equilibrium could now be followed from the opposite side, by observing the pressure built up by decomposition of the oxide. Measurements of the latter kind were repeated at successively higher temperatures. All pressures recorded below are given in mm. of mercury at 0°.

Experimental Results

The results of the final measurements on the dissociation pressure of silver oxide are collected in Table I. The direction in which equilibrium was approached is indicated by the plus or minus sign following the pressures given in Column 2, the plus sign denoting approach from the side of lower pressure, and the minus sign the reverse. In all cases the change of pressure in the last twenty-four hours of observation was less than 0.5 mm. The numerous experiments in which equilibrium was less closely approached will not be detailed here. The values of the average pressure

TABLE I

DISSOCIATION PRESSURE OF SILVER OXIDE

t, °C.	P, mm.			P, av.	$1/T \times 10^4$	Log P
173.0	420.9+	422.9−		422	22.42	2.625
178.0	(514.2−)	511.6±	506.2+	509	22.17	2.707
183.1	607.0−	603.3+		605	21.92	2.782
188.2	713.4+	721.5−		717	21.68	2.856
191.2	790.0±	786.0+		790	21.54	2.898

shown in Column 3 were obtained by weighting all the measurements in accordance with the times of observation.

A plot of the logarithm of the average pressure against the reciprocal of the absolute temperature is shown in Fig. 1. The extreme values of log P indicated at each point show the limits within which the dissociation pressure has been determined with certainty. It will be seen that the observed points lie rather closely on a straight line. A curve very slightly concave toward the axes would fit the observations even better, indicating a very small decrease in the heat of formation with increasing temperature. However, the range of the observations is too small to permit a definite conclusion on this point. From the straight line drawn in Fig. 1 we find for the formation of one mole of silver oxide, $\Delta H_{455} = -7020$ cal. Again because of the short range this value may be in error by as much as 200 cal.

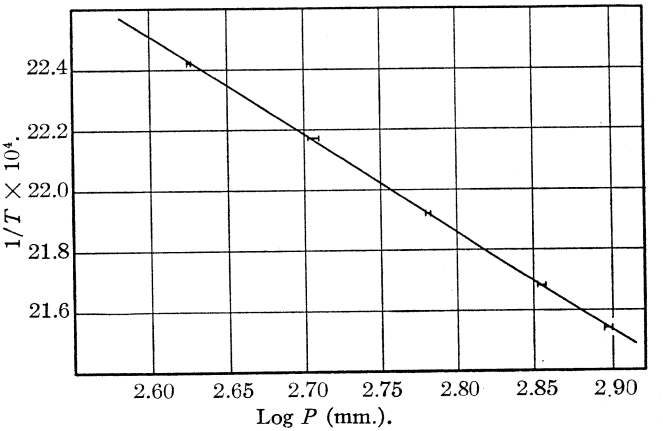


Fig. 1.—The dissociation pressures of silver oxide at 173–191°.

Rate of Attainment of Equilibrium.—The rates of formation and decomposition of silver oxide here observed are very much greater than those found by previous workers. This fact will be evident from Table II, which compares the rate of decomposition obtained by Lewis[2] at 325° with that found by us in an experiment at 173.0° (in this experiment the temperature was 174° for the first forty-nine hours).

TABLE II

RATE OF DECOMPOSITION OF SILVER OXIDE

A. Data of Lewis. Temperature 325°

Time, hrs.	0	12	24	48	72	96	120	144
Pressure, atm.	0	18.5	26.5	29.8	30.1	31.5	31.8	31.8

B. Data of Benton and Drake. Temperature 173.0°

Time, hrs.	0	59	71	99	144	154	168
Pressure, mm.	0	395	402	415	420	421	421

Thus the time necessary to reach apparent equilibrium was approximately the same in spite of the difference in temperature of more than 150°. The much greater reactivity of our sample is doubtless attributable to three main causes: (1) our oxide was prepared synthetically at 170–180° and had never been sintered by heating above 191°, (2) in our sample the original formation of the 9% of oxide presumably occurred in such a manner as to furnish a very large interface between the oxide phase and the unchanged silver—a situation which is known[7] to lead to relatively high rates in reactions of this type, (3) the extended preliminary measurements with our sample, involving repeated formation and decomposition of oxide at low temperatures, would be expected greatly to enhance the reactivity.

We have repeatedly observed that the rate of the reaction in either direction is affected to only a slight extent by the proportion of the silver which is oxidized. Typical data illustrating this point are shown in Table III, which gives the average rate of pressure drop, which is proportional to the rate of formation of oxide, as observed over the range 550-500 mm., with different amounts of oxide already present.

TABLE III

RATE OF FORMATION OF OXIDE AT 173.0°

Oxide present, %	0.7	1.0	5.3
Av. pressure drop, mm. per hr.	2.8	3.3	3.0

It is probable, however, that with substantially larger proportions of oxide there would be less available interface between the solid phases, and slower rates would obtain.

A more detailed discussion of rates and their bearing on the catalytic action of silver in oxidation reactions will be given in a subsequent report.

Discussion

While the results obtained show that a perfectly definite equilibrium is reached in the temperature range 173 to 191°, it is necessary to consider further the nature of the phases present at equilibrium. Since the system is found to be univariant, there must be three phases present—metallic silver, gaseous oxygen and a third phase which is an oxide of silver. It has been found that this oxide is formed from its elements with an evolution of heat which in the above range of temperature is close to 7000 cal. per mole. The averaged value[8] for the heat of formation of ordinary Ag_2O is 6960 cal. at 18° and slightly less at higher temperatures. The agreement of these two heats within the limits of error of our value appears to be conclusive evidence that we are dealing with the ordinary oxide Ag_2O, and not with a possible lower or higher oxide, nor with an allotropic form of Ag_2O. It is of

[7] Lewis, *Z. physik. Chem.*, **52**, 310 (1905). See also Langmuir, THIS JOURNAL, **38**, 2221 (1916).

[8] "International Critical Tables," **5**, 188 (1929).

course possible that both the silver and the oxide might exist in allotropic forms, whose differences in heat content as compared with the ordinary modifications might approximately cancel, but there is no definite evidence of any such allotropes in either case between room temperature and at least 500°. It is probable that the metallic silver phase is in reality a saturated solution of oxygen, or Ag_2O, in silver. However, estimates of the solubility based on the measurements of Steacie and Johnson[9] put the mole fraction of oxygen at these temperatures at not over 2×10^{-4}, so that the heat content and free energy of the silver would not be appreciably affected.

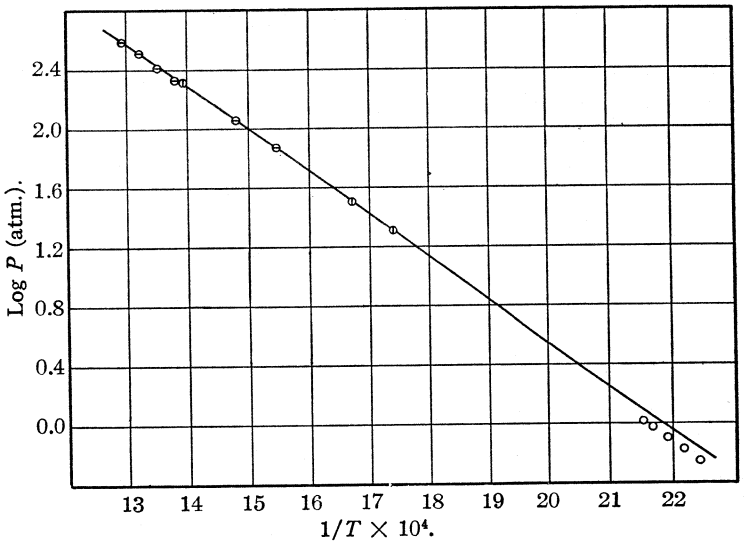


Fig. 2.—Comparison between the pressures observed at 173–191° and those obtained at higher temperatures by Lewis and by Keyes and Hara: ⊖, Lewis; ⊖, K. and H.; ○, B. and D.

The relationship of the data obtained in the range 173–191° to those observed by Lewis[2] and by Keyes and Hara[3] is shown in Fig. 2. The curve there drawn is a plot of the equation employed by Lewis and Randall,[10]

$$\frac{\Delta F^\circ}{T} = -R \ln K = -\frac{7240}{T} - 1.0 \ln T + 21.95$$

It will be seen that our equilibrium pressures are considerably lower than those given by the above equation. At 183.1°, for example, we find a pressure of 605 mm., as compared with 728 mm. from the equation. The temperatures at which the pressure reaches one atmosphere are 190.0 and 184.5°, respectively.

[9] Steacie and Johnson, *Proc. Roy. Soc.* (London), **A112**, 542 (1926).

[10] Ref. 4, p. 481.

Activities at the Higher Pressures.—Comparison of the present data with those obtained in the higher temperature range requires that the latter be corrected for the effect of the high pressures on the activity of each of the three phases. Lewis and Randall[11] have calculated these corrections for two experimental points which lie on the best representative curve. Thus at 598.1°K. they find a corrected pressure of 32.2 atm., compared with 32.0 observed; at 773.3°K. the corresponding values are 392.1 and 388.3. The details of the calculations are not given.

We have repeated these calculations as follows. In the absence of experimental data on the molecular volume of oxygen at temperatures above 200°, we have employed the equation of state for this gas developed by Keyes.[3] For the two points above mentioned, the molecular volumes of oxygen are thus found to be 1547.5 and 186.9 cc., respectively; the corresponding activities a, obtained from the equation $a/P = Pv/RT$, which is a sufficiently close approximation at these temperatures and pressures, are 32.3 and 444 atm. The activities of the silver and silver oxide have been calculated from the equation $RT \ln a = \int_1^P V \, \mathrm{d}P$. The molecular volumes V have been taken as 10.27 for silver and 31.9 for the oxide[12] (the latter being the value derived from x-ray measurements), and both values have been assumed to be independent of temperature and pressure. The activities thus obtained are as follows: for silver, 1.006 at 598.1 and 1.065 at 773.3°K.; for silver oxide, 1.020 and 1.215 at the same two temperatures. A more exact calculation leading to slightly higher values can be carried out in the case of silver by introducing the change of volume with temperature and pressure. However, since the corresponding data are lacking for silver oxide, it seems best to perform the calculation in the same way for both solid phases.

For the reaction $2Ag + {}^1/_2O_2 = Ag_2O$, the true equilibrium constant K is given by the expression $1/K^2 = a_{Ag}^4 \cdot a_{O_2}/a_{Ag_2O}^2$. When the activities given above are introduced, $1/K_{598.1}^2 = 31.8$ and $1/K_{773.3}^2 = 386.9$. These values do not differ greatly from 32.2 and 392.1 calculated by Lewis and Randall. It is difficult to estimate the reliability of these true equilibrium constants, in view of the approximations necessary in calculating the corrections. It appears that the uncertainty at 598.1° is probably very small. At 773.3°, however, the corrections amount to 29% for a_{Ag}^4, 14% for a_{O_2} and 48% for $a_{Ag_2O}^2$. In these circumstances an uncertainty of 5 to 10% in $1/K_{773.3}^2$ appears possible. No corrections are necessary in the case of the data reported in the present paper.

Thermal Data.—The heat of formation ($-\Delta H$) at room temperature of one mole of silver oxide was found to be 5900 cal. by Thomsen, 7000

[11] Ref. 4, p. 480.

[12] "International Critical Tables," 1, 103, 342 (1926).

by Berthelot, and 6800, 7200 and 6300 in calculations by Lewis.[2] The value 5400 obtained by Mixter[13] is certainly too low. The conclusion may be drawn that the true value probably lies between 6300 and 7000. There are no data of any kind for the heat capacity of silver oxide. Application of Kopp's rule suggests that ΔC_p for the formation of one mole of silver oxide at room temperature probably lies between 0 and 2. In the closely analogous case of cuprous oxide the existing data are consistent with the equation, $\Delta C_p = -1.0 + 0.006\ T$.

Comparison of Equilibria in the Two Temperature Ranges.—If ΔC_p is assumed to be independent of temperature, the equilibrium constant K is given by the expression

$$-R \ln K = \frac{\Delta H_0}{T} - \Delta C_p \ln T + I \qquad (1)$$

It is evident from Fig. 2 that the corrected K values at high temperatures are inconsistent with the new results unless ΔC_p exceeds the value 1.0 employed by Lewis and Randall. To bring all the data into agreement on the basis of Equation 1, a value of $\Delta C_p = 3.2$ is necessary, and $-\Delta H_{291}$ would then be 7800 cal. Both these values appear to be too large. The discrepancy is perhaps best appreciated by noting that if the values of $1/K^2$ at 598.1 and 456.2°K. are taken as correct, the average heat of reaction in this range, $\Delta H_{527} = -7050$; thus if ΔC_p is positive, ΔH_{291} must have a larger negative value, and thus lie outside the probable limits of uncertainty.

It does not appear unreasonable to assume that, in analogy with the case of cuprous oxide, ΔC_p increases rapidly with temperature. We find that all the equilibrium measurements can be brought into agreement if $\Delta C_p = -0.494 + 0.006\ T$, so that

$$-R \ln K = -\frac{7610}{T} + 0.494 \ln T - 0.003T + 14.80$$

Nevertheless, $-\Delta H_{291}$ on this basis becomes 7500, which appears too large.

In view of the uncertainty in the heat capacity and heat of formation of silver oxide, and in the calculations of fugacities at the higher temperatures, we conclude that the measurements recorded in the present paper are not necessarily in disagreement with the earlier work. Direct thermal measurements on silver oxide are obviously badly needed.

Because the activity corrections are negligible and the extrapolation to room temperature covers a much shorter interval, the new results are better adapted to a calculation of ΔF°_{298}. If for lack of better values we adopt $\Delta H_0 = -7240$ and $\Delta C_p = 1.0$, as given by Lewis and Randall, our data give the equation

$$\frac{\Delta F^\circ}{T} = -R \ln K = -\frac{7240}{T} - 1.0 \ln T + 21.76$$

[13] Mixter, *Am. J. Sci.*, **32**, 202 (1911).

Thus ΔF°_{298} becomes -2450, which is 2.3% less than the value derived by the above authors, -2395. It must be emphasized however, that a change in ΔC_p can seriously affect the value of ΔF°_{298}.

By combination of ΔF°_{298} for silver oxide with certain other equilibria two methods are available for the calculation of the free energy of formation of water.[4] With the new value for silver oxide the two methods give for the formation of one mole of liquid water $\Delta F^\circ_{298} = -56{,}520$ and $-56{,}580$, respectively. The average, $-56{,}550$, is within 30 cal. of the mean value obtained by three other independent methods, namely, $-56{,}580$.

Summary

1. Metallic silver obtained by low-temperature reduction of the oxide reacts with oxygen at temperatures of 170-200°, forming a definite phase of silver oxide.

2. The equilibrium pressures have been determined in this range of temperature. Values obtained by formation and by decomposition of the oxide agree to within two to four mm., or about 0.5%.

3. The calculated heat of formation is the same within experimental error as that for ordinary silver oxide, Ag_2O.

4. The equilibrium pressures are about 17% lower than those which have been obtained by extrapolation of the results of other workers at 300–500°. This apparent discrepancy is probably to be attributed to uncertainties in the thermal and other data necessary for the extrapolation rather than in the equilibrium measurements themselves.

5. A value of -2450 cal. is calculated for the free energy of formation of one mole of silver oxide at 25°. In spite of the fact that the new data diminish the extrapolation here necessary to a range of 150°, the above figure may be materially affected by the value chosen for the undetermined heat capacity of the oxide.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 305]

SOLUBILITY RELATIONS OF SILVER CHLORIDE IN AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

BY EDWARD W. NEUMAN[1]

RECEIVED DECEMBER 21, 1931 PUBLISHED JUNE 6, 1932

In an earlier article[2] a method was described for the determination of the solubility of inorganic precipitates in aqueous solutions of strong electrolytes. The method was applied to silver chloride in solutions of various nitrates and it was shown that the activity coefficients calculated from the measurements obeyed, at least approximately, the limiting law of Debye and Hückel. The method has here been extended to include solubility measurements of silver chloride in solutions of various valence type sulfates, and the data on some of the nitrate solvent salts, previously investigated, have been extended to higher concentrations.

Theoretical

Solubility measurements are analogous to vapor pressure measurements, in that in one case the solute escapes into a solvent, and in the other into a vacuum. When the solute in the saturated solution is in equilibrium with the solid phase, the activity of the solute in solution is fixed; so that, if foreign substances are added to the solution in equilibrium with the solid, the stoichiometric solubility S may change, but the activity A of the solute must remain constant. Hence for a series of solutions, 0, 1, 2, . . . n

$$A = f_0S_0 = f_1S_1 = f_2S_2 = \ldots\ldots = f_nS_n \qquad (1)$$

where f_1 is the activity coefficient of the solute in a given solution of the system. If f_0S_0 denotes the activity of the solute in the otherwise pure solvent and fS its activity in the same solvent containing also an electrolyte, then, by determining the solubility of the solute at various concentrations of the added electrolyte, it is possible to evaluate f and f_0 from the relation

$$f_0S_0 = fS$$

or, more conveniently[3]

$$-\log f = \log (S/S_0) - \log f_0 \qquad (2)$$

The value of $\log f_0$ may be evaluated by extrapolation, to zero concentration, of a plot of $\log (S/S_0)$ against some linear function of the total concentration.

Debye and Hückel[4] have developed a theory of solutions of strong

[1] National Research Fellow in Chemistry.

[2] Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853 (1930).

[3] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[4] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

electrolytes. Their equation for the activity coefficient of a salt in a solution is

$$-\log_e f_{[1]} = \frac{\alpha(-Z_1Z_2)(\mu)^{1/2}}{1 + a\kappa} \tag{3}$$

Here α is a constant depending on the dielectric constant D of the solvent, the absolute temperature T, and various universal constants, and is defined for decadic logarithms by

$$\alpha = \frac{\epsilon^3(2\pi n)^{1/2}}{2.3026\,(DkT)^{3/2}} \tag{4}$$

The reciprocal of κ is an important quantity in this theory. It has the dimensions of distance and its introduction avoids some of the difficulties encountered by many investigators. It is defined by

$$\kappa^2 = \frac{\epsilon^2\, 4\pi n\mu}{DkT} \tag{5}$$

The quantity a is the distance of closest approach of the ions and is expressed in Ångström units; ϵ is the unit charge in E. S. U., k is Boltzmann's constant; n is Avogadro's number; and μ is the ionic strength of the solution, based on moles per unit volume of solution, and defined by

$$\mu = {}^1/_2 \sum C_i Z_i^2 \tag{6}$$

where C_i is the number of moles per liter of solution, and Z_i is the valence of an ion of the i-th kind. For aqueous solutions at 25°, $\alpha = 0.5066$,[5] and $\kappa = 0.3287^5(\mu)^{1/2}10^8$.

The relation (3) seems to have been generally accepted for aqueous solutions of low valence type salts up to about 0.2μ, but is inadequate for most high valence-type salts and for many non-aqueous solutions. If constancy of the value of a, calculated from the experimental data, be taken as a criterion for applicability of the theory, it will be shown that this relation holds only as a first approximation, if at all, for solutions of a uni-univalent salt in the presence of relatively simple valence-type electrolytes at concentrations as low as 0.002μ. From the form of the equation it may readily be seen that deviations of observed values derived from formula (2), when positive, can only be accounted for in equation (3) by physically absurd negative values of a.

The formula of Debye and Hückel was based on the first approximation of the solution of the Poisson–Boltzmann equation. Gronwall, La Mer and Sandved[6] have succeeded in obtaining a complete solution of this equation. They derived additional terms in powers of a for equation (3) and proposed, for the activity coefficient of a salt, the relation

[5] The numerical values of the constants used in the computation of these factors are: $n = 6.061 \times 10^{23}$; $k = 1.372 \times 10^{-16}$; $T = 298.1$; $\epsilon = 4.774 \times 10^{-10}$; $D = 78.54$. The value for D, the dielectric constant for water, is that given by Wyman, *Phys. Rev.*, **35**, 623 (1930).

[6] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

$$\log_e f_{[5]} = \frac{-\epsilon^2 Z^2 x}{2aDkT(1+x)} + \sum\left[\frac{\epsilon^2 Z^2}{aDkT}\right]^{2m+1} [{}^1/_2 X_{2m+1}(x) + 2m Y_{2m+1}(x)] \qquad (7)$$

where $x = a\kappa$, and κ is defined as in (5). For aqueous solutions[7] at 25° this formula becomes

$$-\log_{10} f_{[5]} = \frac{0.5043(\mu)^{1/2}}{1 + 0.3283a(\mu)^{1/2}} - 0.15382\ F_3(x)10^3/a^3 - 0.007700\ F_5(x)10^5/a^5 \qquad (8)$$

when m is extended to $m = 2$. The first term on the right of equation (7) is the well-known Debye approximation, (equation 3). The X and Y terms are complicated functions of x, and have been evaluated over a wide range of x values. This formula is applicable only to electrolytes of the symmetric valence type in both the solute and the solvent salt and has been evaluated to the fifth approximation.[6]

Recently La Mer, Gronwall and Greiff[8] have extended the treatment to include unsymmetric valence type electrolytes. The computations have been extended to the third approximation. In the case of the activity coefficient of a solute electrolyte in aqueous solution at 25° in the presence of one other electrolyte, their formula becomes

$$-\log_{10} f_{[3]} = -Z_1 Z_2 \left\{\frac{1.53636}{a(1+x)}\, x + \frac{0.12740}{a^2} q_2^2 [{}^1/_2 X_2(x) - Y_2(x)]10^2 + \frac{0.43480}{a^2} q_2(Z_1 + Z_2 - q_2) Y_2(x)10^2 - \frac{0.15382}{a^3} q_2^2 q_3 [{}^1/_2 X_3^*(x) - 2Y_3^*(x)]10^3 - \frac{0.15382}{a^3} q_3^2 [{}^1/_2 X_3(x) - 2Y_3(x)]10^3 - \frac{0.15382}{a^3} q_2[2(Z_1 + Z_2)q_3 + (Z_1^2 + Z_1 Z_2 + Z_2^2)q_2 - 3q_2 q_3] Y_3^*(x)10^3 - \frac{0.30764}{a^3} q_3 [(Z_1^2 + Z_1 Z_2 + Z_2^2) - q_3] Y_3(x)10^3\right\} \qquad (9)$$

The X and Y factors are again complicated functions of x and have been evaluated and tabulated by the authors so that the formula readily yields to computation of values of $\log f_{[3]}$ for comparison with experiment. The factor Z_1 is the valence of the cation, and Z_2 is the valence of the anion of the solute salt. The a value, appearing in Ångström units in the formula, has the same significance as before. In this relatively simple case of only two electrolytes, $q\nu$ has the form

$$q_\nu = \frac{n[\nu_1 Z_1^{\nu+1} + \nu_2 Z_2^{\nu+1}] + n'[\nu_3 Z_3^{\nu+1} + \nu_4 Z_4^{\nu+1}]}{n[\nu_1 Z_1^2 + \nu_2 Z_2^2] + n'[\nu_3 Z_3^2 + \nu_4 Z_4^2]} \qquad (10)$$

wherein n is the number of moles of solute consisting of ν_1 cations of valence Z_1 and ν_2 anions of valence Z_2; and n' is the number of moles of solvent salt consisting of ν_3 cations of valence Z_3 and ν_4 anions of valence Z_4. In

[7] Drude's value for the dielectric constant of water was used [*Ann. Physik*, **59**, 61 (1896)]: $D = 88.23 - 0.4044\ t + 0.001035\ t^2$.

[8] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

the symmetric case of both salts, q_2 is zero and formula (9) simplifies accordingly.

When using the extended formulas for the calculation of a values which are to fit the experimental points, recourse must be had to methods of interpolation, since the forms of the x functions do not readily yield to a direct solution for values of a. Thus, for each total concentration there is a value of κ and a series of x values corresponding to the assumed values of a in Ångström units, for which values the functions $x_2(x)$, $Y_2(x)$, etc., may be found by interpolation on large-scale charts of the tables already computed. The values of $\log f_{[3]}$ or $\log f_{[5]}$ for each assumed a value are then obtained by substitution in formula (8) or (9), as the case may be, and the value of a, corresponding to the experimentally determined $\log f$, obtained by interpolation on the curve $\log f_{[3]}$ or $\log f_{[5]}$ against a.

The formula (9) is given as correct to terms of the third order inclusive. The development is based, in part, on the assumption that $a_1 = a_2 = a_3 = a_4 = a$ in a solution of two electrolytes; that $\log f_{0[3]}$ is equal to $\log f_{0[1]}$; and that there is no specific interaction among the various ions of the two electrolytes such as would result in an alteration of the number of ions from that required by a complete dissociation. This obviates the effects of Bjerrum's[9] ion association and lends the extended theory pertinent significance in view of the theory of complete dissociation of strong electrolytes.

Materials

Water.—Twice distilled, second distillation through a block tin condenser. Specific conductivity, 1.2×10^{-6} mhos. Used in all final recrystallizations, in the preparation of all solutions, and in all experimental work.

Silver Salts.—The nitrate was thrice recrystallized. The sulfate was prepared according to Richards and Jones.[10] During purification and subsequent storage the salts were protected from light as much as possible. As a result no photodecomposition could be noted. Stock solutions were analyzed gravimetrically, and experimental solutions containing 1×10^{-4} mole of Ag^+ per liter were prepared by dilution.

Acids.—Hydrochloric and sulfuric acids were subjected to two distillations retaining only the middle one-third.

Salts.—All salts were carefully purified by two, and in some cases three, recrystallizations. The calcium salts were prepared from pure calcium carbonate. The concentrations of all solutions were checked by analysis. All solutions of the solvent electrolytes were tested for chlorides under the conditions obtaining in the experimental runs. The lanthanum salts were tested for cerium by the hypochlorite method. Only a trace was found in lanthanum chloride and, since the concentration of this salt was never more than 2×10^{-6} M per liter, the effects of cerium salts were disregarded.

Experimental

A series of solutions containing a constant quantity of the solvent electrolyte and varying, but equivalent, amounts of silver nitrate or sulfate

[9] Bjerrum, *Kgl. Danske Videnskab. Selskab, Det, Mathk.-fys. Medd.*, VII, No. 9, 1926.

[10] Richards and Jones, THIS JOURNAL, **29**, 831 (1907).

and the metallic chloride, corresponding to the solvent salt used, were made up in 100-cc. oil sample bottles. The bottles were sealed with corks, which had been soaked in chloride-free paraffin, and were agitated in a water thermostat at 25° until equilibrium was attained. The solutions were examined, at intervals of about eight hours, for turbidity in a Tyndallometer. The standard for comparison was a solution similar in composition to the solutions of the series but containing no silver ions.

The bottles in which the solutions were prepared and examined were carefully selected so that they all had a minimum, and equal, point of reflection when filled with twice distilled water and examined in the Tyndallometer. When used thereafter they were always examined in the calibrated position. The shaker for the bottles was arranged so that the bottles were held upright. This prevented the solutions from coming in contact with the corks and decreased the chances of contamination.

The solutions of the series were measured with calibrated burets. Chloride and silver solutions were measured with micro burets having a capacity of 20 cc. and readable to 0.005 cc. All glass apparatus was washed with cleaning solution, rinsed with distilled water ten times, and finally rinsed five times with redistilled water before use. The temperature of the room was kept at about 25 ± 1° during the preparation.

The solubility of the salt was taken to lie at some point between the concentration showing no turbidity, and the first concentration showing the Tyndall beam. By preparing another series having smaller increments of the concentration of silver chloride and having a range, between and overlapping, for purposes of a more certain control, the last clear and first turbid concentration, it was possible to fix the solubility within still narrower limits. The smallest increments employed at the lowest concentration of solvent electrolytes were 4×10^{-8} M per liter, and 5×10^{-8} M per liter at the higher concentrations. The preliminary series for the approximate location of the point of solubility were usually prepared with increments of 2×10^{-6} M per liter, or more. Table I gives data for one of the experimental points illustrating the preliminary and the final location of the solubility.

TABLE I

DATA ILLUSTRATING METHOD OF OBTAINING THE END-POINT FROM THE TYNDALLOMETER INDICATION

0.001295 M $La_2(SO_4)_3$

Preliminary Series A		Preliminary Series B		Final Series	
Molality of AgCl × 10^5	Turbidity	Molality of AgCl × 10^5	Turbidity	Molality of AgCl × 10^5	Turbidity
1.470	− − − −	1.490	− − −	1.500	− − − −
1.490	− − − −	1.500	− − −	1.505	− − − −
1.510	− + − −	1.510	− − −	1.510	− − − −
1.530	− + + +	1.520	+ + +	1.515	− − + +
1.550	+ + + +	1.530	+ + +	1.520	+ + + +

In series A, the solubility lies between 1.510 and 1.530; in series B, which has narrower limits, the solubility is located between 1.510 and 1.520; and, finally, in the last series having the narrowest limits the solubility is fixed between 1.510 and 1.515.

The criterion for equilibrium was that the Tyndallometer readings became constant. The readings given in Table I extend, for each series, over a period of about seventy-two hours. The first readings were taken at the end of twenty-four hours. It was found that more time was required for the solutions to come to equilibrium in the case of the higher concentrations of the solvent electrolytes. Sulfuric acid proved most troublesome in this respect, and, in addition, the turbidities occurring in solutions of the acid were much less sharply defined than in the case of the salts. Generally, when first prepared, all of the solutions were clear when examined in the Tyndallometer, and in most cases at least twelve hours was required for the first signs of turbidity. In general, solutions that had been cooled until all were turbid, after first having come to equilibrium at 25°, returned to the original state when again agitated in the thermostat at 25°.

The Tyndallometer used for detecting the first appearance of turbidity in the solutions has already been described.[2] Light from a 150-watt, compact-filament tungsten bulb entered the solution through the side of the oil sample bottles. Light, scattered by the solid phase, passed through the bottom of the bottles, whence it was reflected through the optical system of the Macbeth illuminometer and thence to the eye. The illuminometer light was adjusted so that the field of the telescope had a uniform intensity when the standard solution was placed in the apparatus. The color of the reflected light was blue and in order accurately to match the two fields of the telescope it was necessary to insert an appropriate filter in the light path of the illuminometer. Since the amount of solid phase which is formed in the neighborhood of the end-point is necessarily very small, the intensity of the reflected light is very low, necessitating working in a dark room. Occasional solutions which exhibited a relatively bright Tyndall beam were rejected as contaminated and the experiment was repeated.

Data and Discussion

The solubility of silver chloride was determined in aqueous solutions of sulfuric acid, potassium sulfate, calcium sulfate, magnesium sulfate, lanthanum sulfate, potassium nitrate, barium nitrate and lanthanum nitrate. The concentration range covered was from the amount of the solvent electrolyte equivalent to the solute salt, to about 0.04μ, except in the case of calcium sulfate, where the highest concentration was about 0.01μ. The range for potassium and for barium nitrate was from 0.01 to 0.04μ, extending the measurements of Popoff and Neuman. The five lowest points on lanthanum nitrate were measured in the Chemical Laboratory

of the State University of Iowa with the collaboration of Professor Stephen Popoff.

The value of S_0, the solubility of silver chloride in otherwise pure water, can only be obtained by methods of extrapolation from this type of experimental data. This is due to the fact that there is always present, in the solutions, an amount of solvent salt equivalent to the amount of solute salt, or silver chloride. Values of S_0' were determined from the data below 0.01μ for each solvent electrolyte and the results averaged to give the value S_0. The lower portions of the curves S *vs.* $(M)^{1/2}$, where M is the moles of solvent salt per liter of solution, approximated a straight line, and, by assuming the function

$$S = S_0' + A(M)^{1/2} \tag{12}$$

the S_0' values were readily evaluated by the method of moments. Similarly, the values of $\log f_0'$ were determined by assuming the function

$$\log (S/S_0) = (\log f_0') + b(\mu)^{1/2} \tag{13}$$

The arithmetic mean of S_0' and of f_0' was taken as the most probable value of the solubility and activity coefficient, respectively, of silver chloride in water at 25°.

The value of S_0 (mean) is 1.273×10^{-5} as compared to the value of 1.30×10^{-5} mole/liter reported in the "International Critical Tables."[11] Assuming that f_0 (mean) $= 0.9985 = f_+ f_-$ the activity product constant for silver chloride becomes 1.616×10^{-10}.

While not strictly the most accurate method of extrapolation in view of the peculiarities of some of the curves, as will be seen later, the treatment at least eliminates the uncertainties of individual error in graphical extrapolation. The parameters of the statistical equations (12, 13) are given in Table II.

TABLE II

EMPIRICAL PARAMETERS FROM STATISTICAL TREATMENT OF DATA

Solvent electrolyte	$S_0' \times 10^5$	$A \times 10^5$	$A \times 10^5/1.5$	$-\log f_0'$	f_0'	b
HNO_3	1.274	1.527	1.02	0.00075	0.9983	0.5076
KNO_3	1.279	1.455	0.970	.00130	.9970	.5004
$NaNO_3$	1.273	1.540	1.03	.00061	.9986	.5081
$Ba(NO_3)_2$	1.273	2.613	1.74	.00069	.9984	.5005
$La(NO_3)_3$	1.273	3.757	2.50	.00053	.9988	.5045
H_2SO_4	1.268	2.759	1.84	.00023	.9995	.5176
K_2SO_4	1.278	2.687	1.79	.00108	.9975	.5200
$CaSO_4$	1.268	3.406	2.27	.00029	.9993	.5534
$MgSO_4$	1.267	3.430	2.29	.00064	.9985	.5596
$La_2(SO_4)_3$	1.274	6.167	4.11	.00026	.9994	.5141
Mean	1.273	...	..	.00064	.9985	.5186
NO_3^-	1.274	...	..	.00077	.9982	.5042
$SO_4^=$	1.271	...	..	.00050	.9988	.5329

[11] "International Critical Tables," 1929, Vol. VI, p. 256.

The values of b in the last column of the data are analogous to the factor α in the limiting Debye equation, $-\log f = \alpha\mu^{1/2}$, and as such should very closely approximate the value 0.5066, assuming that the dielectric constant of Wyman is correct, and that the limiting law is obeyed in the region below 0.01μ. The average value from the nitrate solvent salts seems to be in good agreement with the theoretical and it might be said that, for the nitrates at least, the limiting law is obeyed below 0.01μ. The mean slope for the sulfates, however, is about 4% higher than the theoretical, a rather significant deviation. The ratios[12] in the middle column, although proportional to the square roots of 1, 3, 4, 6 and 15, in the case of (1, −1), (1, −2), (2, −1), (2, −2), (3, −1), and (3, −2) valence type electrolytes, respectively, have much greater deviations in the case of the sulfates than in the case of the nitrates.

The experimental data appear in Table III. The mean values, $S_0 = 1.274 \times 10^{-5}$ and $\log f_0 = -0.00064$ are used throughout for the calculation of $-\log f$(obs.). The values $-\log f_{[1]}$ were calculated from the limiting law of Debye and Hückel, $\log f_{[1]} = -0.5066\mu^{1/2}$. The apparent ionic diameters $a_{[1]}$ are from the Debye first approximation (3) arranged according to the formula

$$a_{[1]} \text{ (in Ångström units)} = \frac{0.5066\mu^{1/2} + \log f(\text{obs.})}{-\log f(\text{obs.}) \times 0.3287\mu^{1/2}}$$

The apparent ionic diameters, $a_{[5]}$, are obtained to the fifth approximation from the Gronwall, La Mer and Sandved[6] treatment for the case of symmetrical valence type solvent salts, and the diameter $a_{[3]}$ are obtained to the third approximation from the La Mer, Gronwall and Greiff[8] treatment for unsymmetrical cases.

The differences between f(obs.) and f(L.L.) [limiting law] tabulated in the column headed Δ clearly indicate a peculiar mode of deviation from the limiting law. In the case of the unsymmetrical sulfates the change of sign in the deviations is in the order +, −, +, −, with increase in concentration of the solvent salt, and leads to a series of maxima and minima in the experimental curve $-\log f/\mu^{1/2}$, shown in Fig. 1. This phenomenon has not

[12] The value 1.5 is an approximation, for purposes of comparison, of the theoretical parameter A in the equation for the solubility of a slightly soluble (1, −1) salt in a solution of ionic strength μ, given by

$$S = S_0 + A\mu^{1/2} + B\mu + C\mu^{3/2} + \ldots\ldots$$

The terms after the second are assumed to be negligible. The equation may be established from the limiting law and from equation (1) as follows: From (1), $Sf = \zeta$ (a constant), and from the limiting law, $-\log_{10} f = \alpha\mu^{1/2}$, or $f = 10^{-\alpha\sqrt{\mu}}$: then, $S = \zeta 10^{\alpha\sqrt{\mu}}$. Expanding the exponential, we have

$$S = \zeta + \frac{\zeta\alpha \log_e 10\mu^{1/2}}{1!} + \frac{\zeta\alpha^2 (\log_e 10)^2\mu}{2!} + \frac{\zeta\alpha^3 (\log_e 10)^3\mu^{3/2}}{3!} + \ldots\ldots$$

Since S_0 is of the order of 10^{-5}, f_0 is almost unity and the difference between ζ and S_0 may be disregarded for purposes of approximation.

TABLE III

SOLUBILITY RELATIONS OF SILVER CHLORIDE IN AQUEOUS SOLUTIONS OF SULFATES AND NITRATES AT 25°

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[3]}$
		Solvent: Water (by extrapolation)				
1.273	0.	0.003568	0.00064	−0.0027	+	
		(1, −2) Solvent: Sulfuric Acid Solutions				
1.278	0.00000639	0.005652	0.00234	−0.0012	+120	>6
1.289	.00003644	.01106	.00606	+ .0011	− 21	0.8
1.310	.0002065	.02515	.01308	+ .0008	− 3.14	2.53
1.340	.0007067	.04621	.02291	− .0011	+ 1.44	3.86
1.371	.001507	.06734	.03285	− .0026	+ 1.73	2.67
1.384	.002207	.08146	.03695	− .0090	+ 4.37	6.10
1.420	.003107	.09662	.04810	− .0018	+ 0.556	2.70
1.473	.004807	.12017	.06401	+ .0062	− 1.24	3.00
1.485	.005402	.12736	.06754	+ .0059	− 1.07	1.66
1.505	.006484	.13952	.07335	+ .0052	− 0.794	1.78
1.515	.007021	.14518	.07622	+ .0052	− .734	1.72
1.530	.008100	.15594	.08050	+ .0029	− .364	1.85
1.535	.009179	.16599	.08192	− .0041	+ .486	2.22
1.540	.010258	.17578	.08333	− .0108	+ 1.19	2.56
1.552	.010392	.17662	.08670	− .0052	+ 0.552	2.20
1.551	.010794	.18002	.08642	− .0090	+ 0.935	2.37
1.570	.012488	.19356	.09171	− .0117	+ 1.09	2.34
1.580	.013495	.20125	.09447	− .0137	+ 1.20	2.42
		(1, −2) Solvent: Potassium Sulfate Solutions				
1.281	0.000006405	0.005659	0.00336	+0.0011	− 78	0.7
1.291	.00003645	.01106	.00674	+ .0026	− 46	0.4
1.314	.0002065	.02515	.01441	+ .0037	− 14	0.81
1.336	.0007067	.04619	.02162	− .0038	+ 5.42	5.8
1.364	.001507	.06734	.03062	− .0074	+ 5.15	5.9
1.386	.002207	.08146	.03757	− .0077	+ 3.68	4.26
1.413	.003107	.09662	.04595	− .0062	+ 2.06	3.29
1.475	.004807	.12017	.06460	+ .0074	− 1.46	2.94
1.503	.006511	.13984	.07277	+ .0038	− 0.577	1.83
1.526	.008593	.16060	.07936	− .0038	+ .477	2.21
1.550	.010674	.17899	.08614	− .0085	+ .896	2.35
1.576	.013276	.19961	.09337	− .0142	+ 1.27	2.50
		(2, −2) Solvent: Calcium Sulfate Solutions				
1.281	0.000006405	0.00620	0.00336	+0.0005	− 32	0.8
1.287	.00003168	.01128	.00539	− .0014	+ 28.7	>3.
1.306	.0001075	.02105	.01175	+ .0024	− 13.4	0.7
1.344	.0005119	.04539	.02421	+ .0026	− 3.38	1.26
1.372	.001017	.06389	.03316	+ .0017	− 1.13	1.54
1.395	.001522	.07811	.04038	+ .0017	− 0.78	1.62
1.436	.002532	.10070	.05296	+ .0040	− 1.11	1.35
1.467	.002037	.11028	.06224	+ .0129	− 2.82	0.8

TABLE III (*Continued*)

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[5]}$
(2, −2) Solvent: Magnesium Sulfate Solutions						
1.276	0.00000638	0.006188	0.00166	−0.0034	+433.	
1.286	.00003144	.01177	.00505	− .0020	+ 47.	
1.301	.0001065	.02095	.01009	− .0012	+ 7.48	>3
1.319	.0002266	.03118	.01605	+ .0006	− 1.52	1.85
1.340	.0005067	.04517	.02291	+ .0001	− 0.882	2.16
1.377	.0010069	.06357	.03474	+ .0055	− 3.50	1.00
1.402	.0015072	.07774	.04256	+ .0067	− 2.92	1.08
1.438	.0025072	.10022	.05357	+ .0057	− 1.59	1.26
1.454	.0030073	.10974	.05837	+ .0057	− 1.32	1.38
1.489	.005207	.14437	.06870	− .0087	+ 1.36	2.18
1.525	.007608	.17449	.07908	− .0177	+ 2.06	2.52
1.544	.010008	.20012	.08446	− .0315	+ 3.05	2.30
(3, −2) Solvent: Lanthanum Sulfate Solutions						
1.282	0.00000214	0.006702	0.00370	+0.0007	−37	0.8
1.292	.00000660	.01058	.00707	+ .0039	−69	0.95
1.309	.00002440	.01947	.01275	+ .0064	−35	0.75
1.338	.0001033	.03954	.02227	+ .0049	− 7.74	1.60
1.362	.0002467	.06094	.02999	− .0019	+ 1.47	3.20
1.387	.0004132	.07882	.03789	− .0043	+ 2.08	2.98
1.426	.0006690	.10025	.04993	− .0018	+ 0.523	2.39
1.475	.0009589	.12000	.06460	+ .0076	− 1.50	1.72
1.512	.0012950	.13943	.07536	+ .0092	− 1.36	1.42
1.562	.0019048	.16900	.08949	+ .0073	− 0.779	1.42
1.575	.0022853	.18519	.09309	− .0014	+ .129	1.55
1.598	.0026655	.20000	.09939	− .0047	+ .295	1.42
(3, −1) Solvent: Lanthanum Nitrate Solutions						
1.280[a]	0.00000427	0.00620	0.00302	−0.0003	+20	>4
1.305[a]	.00007626	.02169	.01142	+ .0009	− 5.28	3
1.317[a]	.0001438	.02960	.01540	+ .0009	− 2.67	3.02
1.367[a]	.0005780	.05910	.03158	+ .0035	− 2.67	2.39
1.404[a]	.001155	.08333	.04318	+ .0020	− 0.812	2.65
1.432	.001660	.09988	.05175	+ .0024	− 0.677	2.43
1.477	.0028072	.12984	.06519	− .0012	+ 0.212	2.47
1.505	.0038264	.15157	.07335	− .0067	+ 0.941	2.55
1.538	.0051003	.17498	.08277	− .0111	+ 1.23	2.52
1.563	.0066290	.19947	.08977	− .0209	+ 1.92	2.80
(2, −1) Solvent: Barium Nitrate Solutions						
1.450	0.004402	0.11602	0.05718	−0.0032	+0.734	2.56
1.467	.005600	.12967	.06224	− .0069	+1.30	2.95
1.503	.008396	.15875	.07277	− .0147	+2.02	3.10
1.526	.011193	.18328	.07936	− .0255	+2.82	3.56
1.542	.013989	.20490	.08389	− .0379	+3.55	4.07

[a] Values in braces done at State University of Iowa, not published.

TABLE III (*Concluded*)

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[5]}$
(1, −1) Solvent: Potassium Nitrate Solutions						
1.453	0.013695	0.11708	0.05808	−0.0025	+0.550	1.88
1.469	.016431	.12825	.06283	− .0042	+0.808	1.92
1.488	.020064	.14175	.06841	− .0068	+1.086	2.00
1.516	.027376	.16550	.07651	− .0141	+1.76	2.35
1.537	.033760	.18378	.08248	− .0199	+2.15	2.58
1.552	.040144	.20040	.08670	− .0274	+2.59	2.90

hitherto been recorded. The symmetrical sulfates and lanthanum nitrate behave quite differently, the curves exhibiting but one maximum above the

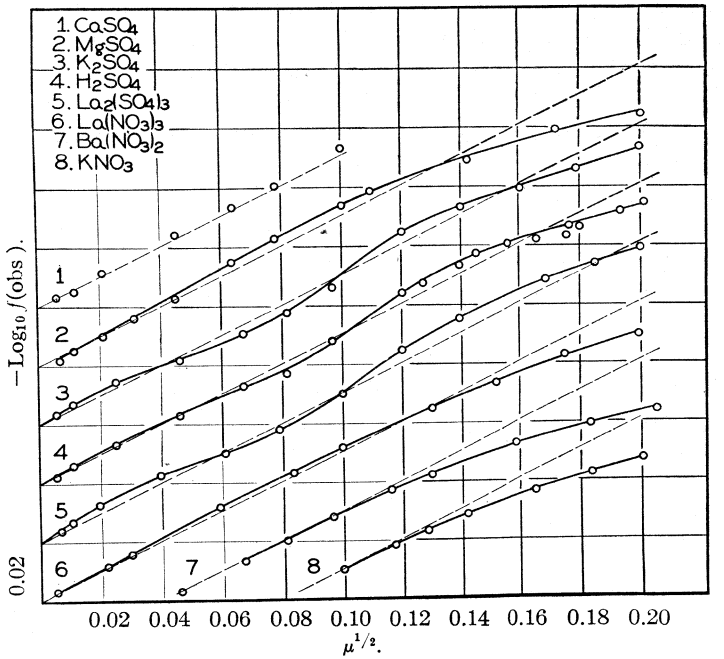


Fig. 1.—Activity relations of silver chloride in aqueous solutions of electrolytes at 25°. The ordinates, $-\log f$ (obs.), have been separated by 0.02 unit (one square). The scale is the same for all curves. 1, Calcium sulfate; 2, magnesium sulfate; 3, potassium sulfate; 4, sulfuric acid; 5, lanthanum sulfate; 6, lanthanum nitrate; 7, barium nitrate; 8, potassium nitrate.

slope of the limiting law. A similar tendency is only very slightly indicated, if at all, in the case of barium and potassium nitrate. "Deviations" of this nature have already been widely noted, chiefly by La Mer and his co-workers.[13]

[13] La Mer and Mason, THIS JOURNAL, **49**, 410 (1927); La Mer and Goldman, *ibid.*, **51**, 2632 (1929).

The characteristics of the curves are clearly illustrated in the graphs of Fig. 1. In this figure the ordinates for each curve, representing $-\log f$(obs.), have been separated 0.02 unit in order to bring out the characteristics of each curve without the confusion of crowding. The scale is the same for all salts and has the same magnitude as the scale of the abscissas. The broken lines represent the slope of the Debye limiting law, and are identical for all of the salts. The points on curves 7 and 8 below 0.1μ are points already published[2] and are here included merely to indicate the degree of agreement of the later data at higher concentrations. The variation in sign is still more strikingly brought out in the $a_{[1]}$ values, a clear indication that the Debye formula fails to apply to the data even in most dilute cases, except as a rough first approximation. The formulas of Gronwall and La Mer are in good agreement with the data. None of the $a_{[3]}$ or $a_{[5]}$ values assume a negative sign and the magnitudes, while small, are not altogether impossible. They exhibit, however, a decided trend in the cases of all of the solvent salts, and the theoretical treatment, in so far as it has been developed, does not account for the first positive and negative "humps" of the unsymmetric sulfate curves. It should be noted, before criticizing the theory too severely, that with decreasing concentration of the solvent salt, very small errors in the value of log f(obs.) are increasingly magnified in the values of "a," whether derived from the Debye theory or from the extended treatments of Gronwall and La Mer.

In Table IV appear the points of maximum and minimum deviation of the experimental curves from the limiting law. These values expressed in $\Delta = \log f$(obs.) $-\log f$(L.L.) were read directly from large scale graphs of the experimental curves appearing in Fig. 1.

TABLE IV

MAXIMUM AND MINIMUM DEVIATION FROM CURVES

Solvent	$\mu^{1/2}$	Δ	Solvent	$\mu^{1/2}$	Δ
H_2SO_4	0.0	0.00	$MgSO_4$	0.00	+ ...
	.03	+ .0008		.04	0.00
	.046	.00		.085	+ .0034
	.08	− .0030		.125	.00
	.107	.00		(0.20)	− .015
	.13	+ .0034			
	.163	.00	$La_2(SO_4)_3$	0.03	+0.003
	(0.20)	− .008		.056	.00
				.082	− .0024
K_2SO_4	0.0	0.00		.103	.00
	.02	+ .0016		.140	+ .005
	.038	.00		.188	.00
	.07	− .0036		(0.20)	− .002
	.103	.00			
	.125	+ .0036	$La(NO_3)_3$	0.04	0.00
	.151	.00		.08	+ .0014
	(0.20)	− .008		.125	.00
				(0.20)	− .0113

Predictions based on the assumption that sulfuric acid is incompletely dissociated, and the calculations of Sherrill and Noyes,[14] would indicate that curve 4 in Fig. 1 should lie somewhat lower than it does. Actually the acid seems to have the same effect as potassium sulfate.

The author wishes to acknowledge the helpful criticism and suggestions of Professors A. A. Noyes and S. J. Bates of the California Institute of Technology, and is indebted to Professor Victor K. La Mer of Columbia University for his valuable criticisms and suggestions in the interpretation of the data.

Summary and Conclusions

The solubilities of silver chloride at 25° in aqueous solutions of the sulfates of hydrogen, potassium, calcium, magnesium and lanthanum, and of the nitrates of potassium, barium and lanthanum, were determined by a synthetic method. The solubility of the chloride in water was approximated statistically and found to be 1.273×10^{-5} mole per liter, and its activity coefficient was found to be 0.9985.

The activity coefficients of silver chloride in the various solutions were calculated from the experimental data. Marked deviations from the Debye–Hückel limiting law as well as from the first approximation formula appear, even at the lowest concentrations, in the case of the sulfates and lanthanum nitrate. The unsymmetric sulfates exhibit positive, negative, positive and finally negative deviations from the limiting law when the logarithm of the observed activity coefficient is plotted against the square root of the ionic strength. The symmetric sulfates show only one such positive deviation, and a similar deviation is barely, if at all, indicated in the case of potassium and barium nitrates.

Apparent ionic diameters, a, calculated on the basis of the Debye first approximation indicate that the theory is inadequate for silver chloride in the presence of the substances studied even at the lowest concentrations. The a values calculated on the basis of the Gronwall and La Mer extensions of the theory are in good agreement with experiment in the case of the symmetrical sulfates and nitrates. These extensions do not explain, however, the peculiar behavior of the unsymmetrical valence type sulfates, except possibly as a first approximation.

PASADENA, CALIFORNIA

[14] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

KINETICS OF A THERMAL CIS-TRANS ISOMERIZATION. II

BY M. NELLES[1] AND G. B. KISTIAKOWSKY

RECEIVED DECEMBER 23, 1931 PUBLISHED JUNE 6, 1932

Isomerization reactions involving a rotation around a carbon double bond have frequently been studied from a chemical point of view. In recent years kinetic studies of the process have been undertaken and some progress in this direction has been made. Most of this work however has been concerned with the photochemical and catalyzed reactions and therefore it need not concern us here.

Höjendahl[2] has studied the thermal isomerization of the maleic into fumaric acid in liquid state. He found a unimolecular reaction with an activation energy of some 15,000 cal. It is somewhat doubtful whether Höjendahl was not dealing with a reaction due to ionic catalysis in view of the low activation energy observed.

Ebert and Büll[3] have announced that measurements on the rate of isomerization of gaseous *cis* and *trans* dichloroethylenes are in progress. They reported that in thermal equilibrium at 300° the mixture contains about 65% *cis* and 35% *trans* compound.

The homogenous isomerization of the dimethyl ester of maleic acid in gaseous state has been recently described by the present authors.[4] The results presented there tend to show that the reaction is of the unimolecular type, although in the pressure range investigated (500 to 45 mm.) the activation rate is insufficient to maintain a unimolecular reaction rate. From the temperature dependence of the rate in the range 270–380°, the activation energy was calculated to be 26,500 cal.

The only secondary reaction which in any way complicated the measurements was a slow decomposition of the fumaric ester formed in the main reaction. The decomposition reaction is accompanied by pressure change, one molecule of carbon dioxide and one molecule of a substance (probably CH_3—CH=CH—$COOCH_3$), which condenses on cooling to room temperature, being formed.

Further experiments seemed necessary to establish more conclusively some of the results obtained. The present paper deals with the reaction rate at pressures above atmospheric, with the influence of inert gases on the rate and with an attempt to determine the position of thermal equilibrium.

[1] Charles A. Coffin Fellow.

[2] Höjendahl, *J. Phys. Chem.*, **28**, 758 (1924).

[3] Ebert and Büll, *Z. physik. Chem.*, **152**, 451 (1931).

[4] Kistiakowsky and Nelles, *ibid.*, Bodenstein Festband, 369 (1931); in the following pages referred to as the first paper.

Experimental Details

The preparation of the materials and the analysis of the reaction mixtures by the freezing point method have been described in the first paper.

A static method was used in the high pressure experiments. Two quartz tubes (capacity 185 and 55 cc.) with heavy walls served as reaction vessels. The following procedure was adopted after several other methods proved unsatisfactory in that they gave unreproducible results. One end of the quartz tube was drawn to a capillary (B in Fig. 1) and the other sealed, through a graded seal, to a T joint. One end of this was connected through a mercury cut-off to the mercury pump and the other ended in a ground joint to which fitted a small tube containing a weighed amount of the ester. The system was evacuated, the ester cooled by carbon dioxide–ether mixture and the quartz vessel degassed at 500–600°. The mercury cut-off was closed, the cooling mixture transferred to the quartz vessel and the ester allowed to distil at room temperature. The quartz vessel was sealed off and placed in a molten lead–tin bath (Fig. 1) for a suitable length of time. It was then quickly cooled by a blast from a carbon dioxide tank. The capillary end of the vessel was attached to a mercury manometer by a cement joint. The manometer was evacuated and the capillary broken by a magnetic plunger while the esters were cooled by carbon dioxide–ether mixture. From the manometer readings and the volume of the system the pressure of carbon dioxide at the end of the heating period could be readily calculated. The liquid products were then analyzed by the freezing point method.

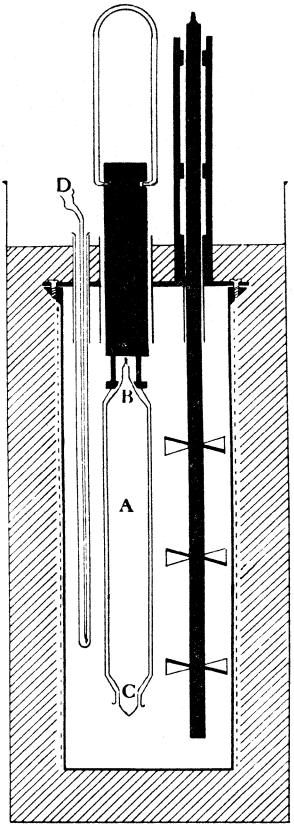


Fig. 1.—The thermostat for high pressure experiments.

The effect of inert gases on the reaction rate was also studied in a static system which is shown in Fig. 2. The ester was introduced through B into C and the former sealed off. The system was then evacuated through A while the ester was cooled by solid carbon dioxide. The inert gas was admitted through a three-way stopcock placed between A and the pump. The system was sealed off at A and the ester vaporized by applying a smoky flame. Finally C was covered with a small electric furnace heated to the temperature of the main furnace. On completion of a run C was cooled and immersed in a carbon dioxide cooling mixture. A rubber tubing attached to the pumps was slipped over A and the tip of this broken with a pair of pliers. The inert gas was slowly pumped out while the ester condensed in C. Appropriate manometer readings were taken to determine the pressure of the inert gas, the total pressure and its change in the course of a run. All gases studied were taken from commercial cylinders. Nitrogen and hydrogen were passed through a purifying train containing a heated tube with copper gauze, wash-bottles with sodium hydroxide solution and sulfuric acid and a tube with phosphorus pentoxide. Propane was purified by passing it through wash-bottles containing fuming sulfuric acid, dilute sulfuric acid alkaline potassium permanganate and concentrated potassium hydroxide solution. After drying over phosphorus pentoxide it was fractionated several times in vacuum. Carbon dioxide was subjected only to a repeated fractional sublimation in vacuum. With the last two

gases it was found that a very thorough purification was required, quite erratic results being obtained otherwise.

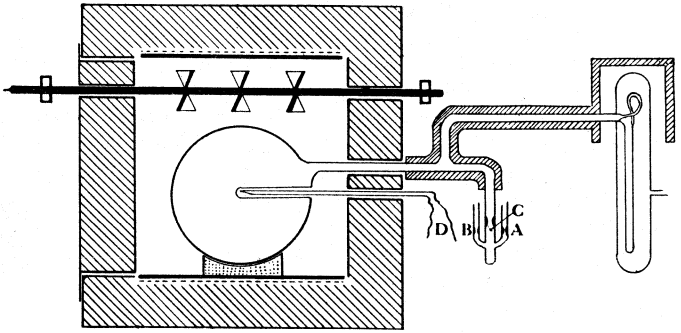


Fig. 2.—The apparatus for low pressure experiments.

Experimental Results and Discussion

Table I presents the results of the final series of experiments on the rate at high pressures.

TABLE I

No.	T, °K.	Time, minutes	p, mm.	Δp, mm.	Fumaric ester, % By analysis	Fumaric ester, % Corrected	K min.$^{-1}$ $\times 10^4$
1	573	122	732	34.5	11.2	15.9	2.67
2	573	108	731	40.0	8.5	14.0	2.63
3	573	121	731	32.4	10.8	15.2	2.58
						Av.	2.62
4	573	60	2140	30.0	12.0	13.4	4.52
5	573	60	2139	31.2	11.8	13.4	4.52
6	573	62	2142	27.8	13.2	14.5	4.75
						Av.	4.57
7	573	30	4070	32.4	7.8	8.6	5.65
8	573	45	4060	44.0	9.4	10.5	4.65
9	573	45	4060	46.2	3.6	10.7	4.74
						Av.	5.01

In column 5 is given the amount in mm. of carbon dioxide formed at the temperature of the experiment. It was set equal to the amount of fumaric ester decomposed and added to the fumaric ester found by analysis in calculating the rate constants. The rest of the table is self-explanatory. It will be noticed from these data that with increasing pressure the rate tends to become unimolecular. This is particularly well shown by Fig. 3, in which the new data as well as those obtained previously (I) have been plotted. The velocity constant at 45 mm. pressure has not been included in Fig. 3 in order not to reduce the scale of the drawing too much. This constant does not fall on the straight line drawn, being about 30% too high. The measurements at this pressure, however, were rather unsatis-

factory due to large percentage decompositions of fumaric ester and little weight should be attributed to this discrepancy. The rest of the points in Fig. 3 fall very near a straight line calculated from the equation

$$K_{573^\circ} = \frac{7.7 \times 10^{-4}}{1 + \frac{1400}{P_{\text{mm.}}}} \text{ min.}^{-1} \qquad (1)$$

showing that the reaction is indeed of unimolecular type.

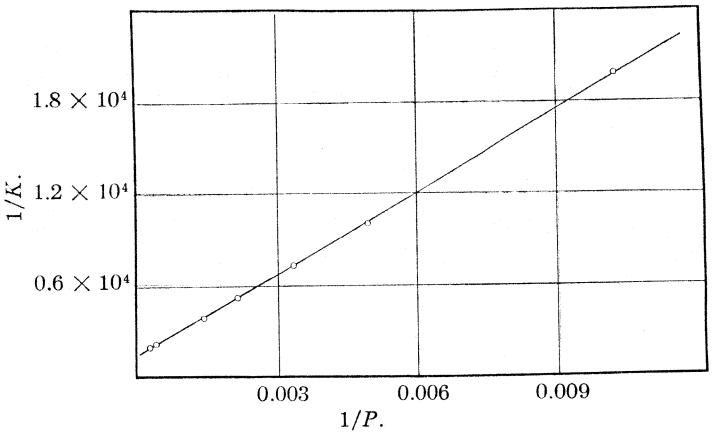


Fig. 3.—A plot of inverse velocity constants against inverse pressure.

In Table II are presented experiments dealing with the action of inert gases.

TABLE II

EXPERIMENTS WITH INERT GASES

No.	T, °K.	Time, minutes	Pressure, mm.	Total pressure	Δ pressure	Fumaric ester, % By analysis	Corrected	K × 10⁴
				No added gas				
19	593	56	110		1	3.0	3.9	6.71
18	593	126	108		1	6.7	7.7	6.38
20	593	177	112		1	11.1	12.0	7.20
21	594	234	108		2	14.9	16.9	7.91
								7.05 at 593°
				Hydrogen 250 mm.				
118	591	93	110	360	1.5	5.2	6.6	6.65
119	588	63	110	360	1.0	3.0	3.9	6.35
120	588	84	110	360	1.4	4.4	5.7	7.00
								6.65 at 588°
				Hydrogen 500 mm.				
121	588	66	114	614	1.0	4.4	5.3	8.80
122	591	63	120	620	1.1	4.0	4.9	7.72
123	589	92	112	612	1.2	5.5	6.6	7.76
								8.1 at 590°

TABLE II (*Concluded*)

No.	T, °K.	Time, minutes	Pressure, mm.	Total pressure	Δ pressure	Fumaric ester, % By analysis	Fumaric ester, % Corrected	$K \times 10^4$
				Nitrogen 250 mm.				
111	595	71	110	360	1.2	4.0	5.1	7.14
113	594	37	109	359	0.6	2.4	2.9	7.84
114	599	79	113	363	1.4	4.7	6.0	6.60
								7.22 at 594°
				Nitrogen 500 mm.				
115	592	47	112	616	0.9	1.7	2.5	5.66
116	593	82	111	611	1.6	3.5	5.0	6.27
117	593	39	112	612	0.8	1.4	2.1	5.50
								5.81 at 593°
				Propane 500 mm.				
170	591	60	164	664	2.5	8.1	9.6	16.9
171	592	58	113	613	2.5	6.1	8.3	15.2
172	591	62	126	626	1.4	6.7	7.8	13.5
								15.2 at 591°
				Carbon Dioxide 500 mm.				
127	591	61	112	612	6.8	10.7		18.6
128	591	29	107	607	5.3	16.4		22.5
								20.5 at 591°

Hydrogen and nitrogen are both found to be without influence on the reaction. Propane has a feeble accelerating action, equal to about one-tenth of the effect of the esters themselves. The effect of carbon dioxide is more pronounced. It is obscured somewhat by a rapid decomposition of the esters induced apparently by carbon dioxide. Because of this the isomerization rate constants have been calculated here neglecting the decomposition reaction. They represent therefore the minimum values of the acceleration produced. Inasmuch as it is not known whether fumaric ester alone or maleic ester also decomposes in presence of carbon dioxide, a more accurate calculation is impossible.

Some experiments have been carried out to determine the position of thermal equilibrium. The decomposition of fumaric ester precludes the study of equilibrium by the usual methods. The procedure adopted was to heat known mixtures of the esters for a short time and to determine the change in the freezing point. It was found that at 280° the freezing point remained unchanged in a 1 : 1 mixture. It was lowered in mixtures richer in fumaric ester and raised in mixtures richer in maleic ester. On studying the temperature dependence of this apparent equilibrium over the range 255–320°, the following expression was found to represent it approximately

$$\ln K = \frac{6000}{RT} - 5.5$$

Such a large entropy change in a reaction of the present type seemed to be quite unlikely and suggested that the equilibrium was fictitious. Further experimentation showed indeed that the liquid formed on heating fumaric ester was not maleic ester. The lowering of the freezing point is due therefore chiefly to decomposition reactions. Although this finding precludes an accurate determination of the equilibrium, still the conclusion can be reached that in the true state of equilibrium more than 50% of fumaric ester is present. This is to be compared with the observation of Ebert and Büll that, of the two dichloroethylenes, the *cis* modification is the more stable one.

It has been pointed out in the first paper that the isomerization process is unusually slow as compared with other unimolecular reactions. The measured rate of activating collisions, equal to the reaction rate at low pressures, is of the order of $10^{28}\, e^{-24,500/RT}\, c^2$ (c, concentration in moles per liter). The rate of collisions with energy in excess of 26,500 cal. contained in two square terms is about $7 \cdot 10^{31}\, e^{-24,500/RT}\, c^2$. Experiments at higher pressures indicate that the limiting velocity constant at infinite pressure is

$$K_\infty = 1.3 \times 10^{5}\, e^{-26,500/RT} \text{ sec.}^{-1}$$

Usually the temperature independent factor is at least of the order of 10^{10}. The other unimolecular reactions which have activation rate not exceeding the rate of collisions with energy contained in two square terms are the decompositions of nitrous oxide[5] and of nitryl chloride.[6] As both these molecules consist of only very few atoms, a much greater rate could hardly be expected. The decompositions of larger molecules, studied thus far, all require the assumption of internal energy exchange between several degrees of freedom. It has been noticed, however,[7,8] that most frequently not all degrees of freedom, available from the point of view of specific heats, participate in the reaction. The barriers which partially prevent energy exchange within the molecules must be particularly effective in the isomerization process, as shown by the present measurements. This should be attributed to the character of mechanical motion responsible for the reaction: a rotation of heavy atomic groups around the double bond instead of the longitudinal vibrations active in decomposition processes. From this point of view it is comprehensible also that only heavy molecules like carbon dioxide and propane are able to participate in the activation process of the isomerization, while in decomposition reactions of organic molecules hydrogen seems to participate more readily than any other molecule.

[5] Volmer, *Z. physik. Chem.*, **9B**, 141; **10B**, 414 (1930).

[6] Schumacher and Sprenger, *ibid.*, **12B**, 112 (1931).

[7] Rice, *ibid.*, **7B**, 226 (1930).

[8] Ramsperger and Leermakers, THIS JOURNAL, **53**, 2061 (1931).

In view of the slowness of the activation rate, it could be assumed that energy is transferred in collisions directly to the oscillatory motion around the double bond. When energy in excess of 26,500 cal. has been accumulated, free rotation results. On the next inelastic collision accompanied by energy loss a maleic or fumaric ester molecule is formed depending on the orientation of the two rotating halves of the molecule in the instant of collision. The relative yields of the two are determined by the average times spent by the rotating molecule in the *cis* and the *trans* configuration. There are no grounds to assume that the times spent in either form differ considerably and therefore about a 50% yield of fumaric ester should be expected. On the basis of this mechanical model the gradual falling off of the reaction rate, as compared with activation rate, with increasing pressure is due to the fact that some molecules lose their energy before carrying out a 90° rotation. A considerable difficulty appears, however, if this assumption is made. It will be noticed from equation (1) that half of all activated molecules lose their energy, before free rotation has been established, at 1400-mm. pressure. The collision frequency at this pressure is about 10^{11} sec.$^{-1}$. Activation occurs on less than one in a thousand possible collisions and, since the statistical energy distribution must be maintained, the same is true of deactivation. Therefore the average time between activation and deactivation is of the order of 10^{-8} sec. This is a considerably longer time interval than the likely period of a rotation. Thus the possibility must be considered that some time elapses between the instant of the activating collision and the setting in of free rotation. This would occur if the energy was first transferred to some other mode of motion within the molecule and only later supplied to the rotation around the double bond. A proposal of this kind, while eliminating one difficulty, is not entirely satisfactory in that it obscures the cause of the exceptional slowness of energy exchange between ester molecules and also the lack of energy exchange with any but heavy inert gas molecules. Experiments on other esters of maleic acid, now in progress in this Laboratory, will perhaps settle this problem.

The position of equilibrium with dichloroethylenes as determined by Ebert and Büll[3] shows that dipole interaction in these molecules is quite small. In dimethyl esters of maleic acid the interaction should be even weaker on account of larger distance between the dipoles. It is thus apparent that the activation energy observed (26,500 cal.) represents almost exclusively the straining of the double bond on a 90° rotation of the two atomic groups composing the molecule.

Summary

1. The rate of homogenous isomerization of gaseous dimethyl maleic ester into dimethyl fumaric ester has been studied at pressures up to 5

atm. and also in the presence of hydrogen, nitrogen, propane and carbon dioxide.

2. The variation of the velocity constant with pressure can be represented by the equation

$$K_{575^\circ} = \frac{7.7 \times 10^{-4}}{1 + (1400/P)} \text{ min.}^{-1}$$

from which the limiting value at infinite pressure is obtained to $K_\infty = 1.3 \times 10^5 \, e^{-26500/RT}$ sec.$^{-1}$.

3. Hydrogen and nitrogen have no effect on the reaction velocity, while propane and carbon dioxide accelerate it.

4. In the thermal equilibrium the ratio of fumaric to maleic ester is greater than unity.

5. The slowness of the activation process in the reaction is discussed and is linked to the nature of the mechanical motion responsible for the reaction.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

THE PREPARATION AND PROPERTIES OF TITANIUM TETRABROMIDE AND TITANIUM TRIBROMIDE HEXAHYDRATE[1]

BY JOHN C. OLSEN AND EMMETT P. RYAN

RECEIVED DECEMBER 26, 1931 PUBLISHED JUNE 6, 1932

Very few of the salts of titanium have been prepared in pure form and their properties studied. Considerable work has been done at the Polytechnic Institute on titanium compounds. As a part of this research titanium tetrabromide and titanium tribromide hexahydrate have been prepared and studied.

Duppa[2] prepared the tetrabromide and describes it as an amber-yellow substance, attracting moisture with the greatest avidity and being converted into titanic and hydrobromic acids, boiling at 230° and melting at 39°. Thorpe[3] describes it as a dark yellow or orange crystalline mass melting at about 40° and boiling at 229° uncorrected. Its density is reported as 2.6 by Duppa and 3.37^{25}_{4} by Klemm, Tilk and Müllenheim.[4]

Preparation of Titanium Tetrabromide.—The tetrabromide was prepared in three ways.

[1] From the thesis submitted in partial fulfilment of the requirements for the degree of Master of Science by Emmett P. Ryan. This paper was read at the Buffalo Meeting of the American Chemical Society, August 30–September 4, 1931.

[2] Duppa, *Proc. Roy. Soc.* (London), **8**, 42 (1857).

[3] Thorpe, *J. Chem. Soc.*, **47**, 126 (1885).

[4] Klemm, Tilk and Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 1–22 (1928).

(1) **A Modification of Duppa's Method.**—An intimate mixture of pure titanium dioxide and carbon black was placed in an inclined 25-mm. Pyrex tube. By means of a two-way stopcock, carbon dioxide, dry and free from oxygen, was passed either directly into the reaction tube or first into a flask containing bromine, heated to 60° to increase its vapor pressure. The tube was heated and swept free from air and moisture by the carbon dioxide after which the stopcock was turned and the bromine-saturated gas passed over the mixture of titanium dioxide and carbon heated to 640°. Titanium tetrabromide, carbon tetrabromide and excess bromine collected in the distilling flask at the end of the tube. The bromine was removed by distillation on a water-bath in a stream of carbon dioxide, and the carbon tetrabromide by later distillation. The titanium tetrabromide remained in the flask as an amber-yellow solid at room temperature. It was purified by distillation as described later.

(2) **Thorpe's Procedure.**—Hydrogen bromide was passed into titanium tetrachloride heated just below its boiling point. The hydrogen bromide, prepared by the action of bromine on red phosphorus and water, was freed from entrapped bromine fumes by passing through a U-tube filled with glass wool and red phosphorus, and dried by passing over soda lime. The hydrogen bromide was passed intermittently for thirty hours before the boiling point of the contents of the flask rose from that of titanium tetrachloride, namely, 136.4, to 228°, the boiling point of titanium tetrabromide. The hydrogen bromide was passed for five hours more, the boiling point remaining constant. This product was also purified by distillation.

(3) **Ruff and Eisner's Method.**[5]—This method is similar to (1) except that titanium carbide was used in place of titanium dioxide and carbon black. This method was abandoned after one run because we were unable to secure an iron-free sample of titanium carbide. Thorpe's method requires the longest time but gives the purest product. A large quantity can also be most easily prepared by this method. Sixty grams was made by Duppa's method in two runs, while 450 g. was made by Thorpe's method in one run.

The titanium tetrabromide made by either method was twice distilled in an atmosphere of dry carbon dioxide, collecting that portion boiling at 228° uncorrected. Samples were collected in constricted glass tubes. The air was displaced by dry carbon dioxide and the bromide distilled into the tubes, which were immediately sealed off at the constriction.

The tetrabromide was analyzed by carefully breaking these tubes under water acidulated with a small amount of nitric acid. This was made up to a known volume and aliquot portions were withdrawn. The bromine was precipitated with silver nitrate and weighed as silver bromide. The titanium was precipitated with ammonium hydroxide and weighed as titanium oxide after bringing to constant weight over a Méker burner.

Anal. Calcd. for $TiBr_4$: Ti, 13.03; Br, 86.97. Found: Ti, 13.21, 13.19, 13.30; Br, 86.62, 86.76.

The properties as determined were found to be as follows. Titanium tetrabromide is readily and completely soluble in 34% hydrobromic acid at room temperature and also in concentrated hydrochloric acid.

Concentrated nitric acid decomposes it. Nitrogen peroxide is given off, bromine settles to the bottom of the tube and titanic acid remains in solution.

Concentrated sulfuric acid decomposes the tetrabromide, liberating hydrogen bromide. Part of the hydrogen bromide reacts with the excess sulfuric acid forming bromine, water and sulfur dioxide. A reddish-brown solution is formed.

[5] Ruff and Eisner, *Ber.*, **41**, 2260 (1908).

Ammonium hydroxide and a 20% aqueous solution of sodium hydroxide decompose the tetrabromide, forming a heavy white precipitate of $Ti(OH)_4$. The reaction is analogous to that of ammonium hydroxide on titanium tetrachloride, forming a precipitate of $Ti(OH)_4$.

Titanium tetrabromide is soluble in chloroform, carbon tetrachloride, absolute ether and absolute alcohol.

Quantitative Determination of the Solubility of Titanium Tetrabromide in Alcohol and Ether.—Titanium tetrabromide was distilled in a stream of dry carbon dioxide into a small flask which was quickly stoppered. A quantity of alcohol or ether, insufficient to dissolve the tetrabromide, was added. The flask was allowed to stand overnight. It was then brought to 20° and kept there for two hours with frequent shaking. A portion of the supernatant liquid was drawn off into a pycnometer and weighed at 20°. The contents was dissolved in water and the bromine content determined.

Two hundred and eighty-seven grams of titanium tetrabromide is soluble in 100 cc. of absolute alcohol at 20°. The density of this solution is 2.29_4^{20}; 3.6 grams of titanium tetrabromide is soluble in 100 cc. of absolute ether at 20°.

Density.—As titanium bromide is hydrolyzed by water, mercury was used for the determination of density. A sample of titanium tetrabromide was distilled in an atmosphere of carbon dioxide and collected in a small test-tube drawn out near the top. On cooling, the tetrabromide solidified in the bottom of the tube and adhered firmly to the tube which was then sealed. The narrow portion of the tube was marked with a file in two places about an inch apart and the tube weighed. At the upper of the two file marks the tube was broken under mercury and filled, the temperature brought to 20° and the mercury level adjusted to the mark. The tube and contents were then weighed. The tube was now cleaned out, dried, and weighed with the glass tip broken off from the tube on filling. Its weight filled to the mark with mercury at 20° was then found. The density of the tetrabromide was 3.23_4^{20}.

The density was also determined in a vacuum. The sample was prepared as before but now the tetrabromide was but little more than covered with mercury. It was placed in a vacuum in a desiccator to wet the surface of the sample thoroughly. The tube was then removed from the desiccator, filled to the mark with mercury at 20° and weighed. The density was 3.25_4^{20}.

Duppa gives 2.6 as the density and Klemm, Tilk and Müllenheim 3.372_4^{25}. Duppa, who was the first to prepare titanium tetrabromide, does not give his method of determining the density. Handbooks have evidently taken his figure. Klemm, Tilk and Müllenheim give their method. They took especial care before filling the tubes up to the mark with mercury to place them under high vacuum to remove (as they state) any moisture that may have entered while getting the samples in the tubes. As moisture rapidly hydrolyzes titanium tetrabromide to hydrogen bromide and titanium dioxide, part of the tetrabromide would be hydrolyzed before the moisture could be removed by vacuum. As titanium dioxide has a density of from 3.75 to 4.25 any of this oxide formed would give high results especially where small samples were taken. The samples used for the two determinations which they made weighed 0.5943 and 0.3889 grams.

In filling our sample tubes, the tetrabromide was distilled in an atmosphere of dry carbon dioxide into dry test-tubes from which the air

had been displaced by carbon dioxide. They were then sealed off from the air and broken under mercury. Furthermore, samples of 8.3450 g. and 5.2538 g. were used. For these reasons we believe 3.24_4^{20}, the average of our two determinations 3.25_4^{20} and 3.23_4^{20}, more accurate than the 3.37_4^{25}, the average of Klemm, Tilk and Müllenheim's two determinations, 3.36_4^{25} and 3.38_4^{25}. Duppa's results are obviously low.

Titanium Tribromide Hexahydrate.—Stähler[6] prepared titanium tribromide hexahydrate by electrolyzing a solution of titanium tetrabromide in hydrobromic acid. He describes the crystals as dark violet, intermediate in stability between the corresponding chloride and iodide and deliquescing in air to a brown, strongly fuming liquid. We prepared the hydrated tribromide in a similar manner and present the following additional data.

Preparation.—Twenty-six grams of titanium tetrabromide was dissolved in 23 g. of 34% hydrobromic acid and placed in a porous cup 41 mm. in diameter and 76 mm. in height. This was placed in a 400-cc. beaker containing 34% hydrobromic acid. The liquids in the porous cup and beaker were kept at the same level. Two carbon rods served as the electrodes, with the porous cup as the cathode compartment. A current of 2.5 amperes was passed through the solution for two hours. When dry hydrogen bromide gas was passed into the ice cooled flask containing the violet colored solution, crystals of hydrated titanium tribromide separated out. The crystals were filtered on Gooch asbestos, washed with ether, and dried in a desiccator over soda lime until constant. The following analysis indicates that the crystals were very nearly pure $TiBr_3 \cdot 6H_2O$.

Anal. Calcd. for $TiBr_3 \cdot 6H_2O$: Ti, 12.10; Br, 60.58; $TiBr_3$, 72.69. Found by gravimetric analysis: Ti, 12.16, 11.75; Br, 59.52, 59.24; $TiBr_3$, 71.68, 70.99.

Properties.—Titanium tribromide hexahydrate is a light reddish-violet crystalline substance. It deliquesces in air to a heavy brown liquid but may be kept in a desiccator over soda lime, with but slight decomposition. The crystals melt at 115.0°.

It is soluble in water giving a violet color in concentrated solutions, and is soluble in hydrobromic acid giving a brownish solution.

Titanium tribromide hexahydrate is also soluble in methyl alcohol, absolute ethyl alcohol, and acetone, insoluble in carbon tetrachloride and benzene, and decomposes on standing with absolute ether.

Summary

Titanium tetrabromide was prepared by three methods. It is soluble in chloroform, carbon tetrachloride, absolute ether, absolute alcohol and hydrobromic and hydrochloric acids. It is decomposed by nitric acid, sulfuric acid, ammonium hydroxide and an aqueous solution of sodium hydroxide; 287 g. of titanium tetrabromide is soluble in 100 cc. of absolute alcohol at 20° and 3.6 g. in 100 cc. of absolute ether at 20°. The correct density determination is 3.25_4^{20}.

Titanium tribromide hexahydrate was prepared. It melts at 115°. Solubilities in various solvents and other properties are given.

BROOKLYN, NEW YORK

[6] Stähler, *Ber.*, **37**, 4409 (1904).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 304]

STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. I. THE PRECIPITATION BY AMMONIUM HYDROXIDE

BY ERNEST H. SWIFT AND R. C. BARTON

RECEIVED JANUARY 2, 1932 PUBLISHED JUNE 6, 1932

Introduction

During the course of an attempt to develop a system of qualitative analysis for the so-called common elements which would provide more quantitative information than that usually obtained, it became one of the first problems to examine the methods commonly used for the qualitative separation of these elements into groups. The extensive investigations of Noyes and Bray and their co-workers[1,2,3] have furnished much information as to the qualitative value of many of these separations, with special reference to the detection of very small amounts of one element in the presence of large amounts of the other, but very little information with respect to the completeness of the separation when each element is present in moderate or large amounts. Although these same separations are used in quantitative methods, surprisingly little systematic information of this nature seems to be collected in texts or reference works; while that in the original literature is widely scattered, gathered under such varying conditions as to be difficult to correlate, and apparently quite incomplete. Therefore it has seemed worth while to present the results of these studies in this series of papers.

The Precipitation by Ammonium Hydroxide.—The precipitation by ammonium hydroxide can well be termed one of the classical analytical separations and, as is stated by Hillebrand and Lundell,[4] "One of the commonest operations the analyst has to perform ..., with the object either of weighing the precipitated compound or of effecting a joint separation of two or more metals from others." That it may be inadequate even as a qualitative separation in certain cases is shown by the experiments of Noyes and Bray[5] in which, with large amounts of aluminum or ferric iron (100–200 mg.) and with amounts of cobalt, zinc or nickel up to 20 mg., from 75 to 99% of the latter elements were found to be carried down

[1] Noyes and Bray, THIS JOURNAL, **29**, 137 (1907).

[2] Noyes, Bray and Spear, *ibid.*, **30**, 481 (1908).

[3] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927.

[4] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. 69.

[5] Ref. 3, pp. 153–155.

in the precipitate. Noyes, Bray and Spear[6] also state that "a large quantity of zinc may be quantitatively precipitated by ammonium hydroxide when a larger proportion of chromium is present; and manganese will in any case be partially precipitated by that reagent owing to its oxidation by the air." In a careful study of the conditions necessary for securing complete precipitation of aluminum by ammonia, Blum[7] has found that these are attained by carefully neutralizing the solution, using methyl red (or rosolic acid) as indicator, and avoiding an excess of ammonia. Concerning its separation from other elements the following statement is made: "It is well recognized that the separation of aluminum from such elements as zinc, manganese, nickel and cobalt by means of ammonia is unsatisfactory since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminum hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of the manganese occurred so rapidly as to preclude a quantitative separation."

However, Lundell and Knowles[8] in an extensive series of experiments, in which the precipitations were carried out according to the procedure developed by Blum,[7] show that moderate amounts of iron and aluminum can be separated from manganese and nickel quite satisfactorily; under the same conditions considerable amounts of cobalt, copper and zinc were found in the precipitates. It was also found that an excess of ammonia, although apparently improving the separation of aluminum and iron from copper and zinc, made the separation of these two elements from manganese, nickel and cobalt less satisfactory. The striking experiments of Noyes and Bray, cited above, in which a relatively large excess of ammonia was present, seem to confirm this latter observation and to raise considerable question as to whether a more effective separation is obtained by having an excess of ammonia present. This would seem to depend upon whether the bivalent elements remain in solution due to the solubility of their hydroxides (as is most probable with manganese) or due to the formation of the soluble ammonia complexes, and, furthermore, to the relative tendency of these two molecular types to be carried down with the precipitate. The effect of the P_H of the solution upon the adsorbing tendency of the precipitate has also to be considered. In spite of this uncertainty, the proper attention apparently has not been given, in qualitative procedures (or in quantitative methods where the complete precipitation of aluminum is not involved), to the effect of making a careful neutralization or of exactly adjusting the excess of ammonia. It will be shown in the experiments to be presented that the proper control of the excess of am-

[6] Ref. 2, p. 482.

[7] Blum, THIS JOURNAL, **38**, 1291 (1916).

[8] Lundell and Knowles, *ibid.*, **45**, 676 (1923).

monia is a most important feature in the separations which have been included in the present investigation, and that many of these separations are quite inadequate even for crude qualitative separations unless the neutralization with ammonia is carefully performed.

This study has been restricted mainly to the elements iron, aluminum, chromium, manganese, nickel, cobalt and zinc; however, since in the qualitative analysis of the common elements, the ammonium hydroxide separation is likewise used to separate bismuth from copper and cadmium, a few experiments are shown to indicate the sharpness of these separations. The effect of phosphate has not been included in this paper. It has not seemed worth while to give separate references to all of the previous work dealing with each of the individual separations here studied. In most cases these can be found, with a brief discussion, in the reference work of Rüdisüle.[9]

Experimental Procedure

The separations were carried out according to three general procedures. The first of these, designated Procedure I, was designed to conform to usual qualitative technique, and, except where explained by notes, was as follows.

To a boiling solution containing the elements to be separated and 60 milli-equivalents of hydrochloric acid in a volume of 100–125 ml., 6 normal ammonium hydroxide was slowly added until red litmus paper just turned a distinct blue color. The mixture was then boiled for one to three minutes and filtered; it was kept hot during the filtration. The precipitate was washed with hot water until the washings were colorless or had no perceptible effect on red litmus.

Procedure II, conforming more closely to the procedure outlined by Blum, was as follows.

To a boiling solution, which contained 10 g. of ammonium chloride and 6–12 milli-equivalents of hydrochloric acid in a volume of approximately 250 ml., 6 normal ammonium hydroxide was added dropwise until a color change was noted using methyl red, or in a few cases rosolic acid, as the indicator. Where the color of the solution prevented the use of the internal indicator, litmus test papers were used and the ammonia added until the color of the litmus matched that obtained from a similar solution of ammonium chloride and hydrochloric acid to which ammonium hydroxide had been added until the methyl red (or rosolic acid) color transition occurred. Extreme care was taken in these neutralizations; if the color transition was over-run, the mixture was made acid and the process repeated. The mixture was boiled for one to two minutes and filtered; it was kept hot until the filtration was completed. To expedite filtering and washing two separate filters were used in most cases. The precipitate was washed with a hot 2% solution of ammonium chloride until the washings gave no appreciable precipitate when tested with ammonium sulfide solution.

Procedure II differs from Procedure I in that the solution was diluted to a larger volume, a larger quantity of ammonium chloride was present and extreme care was taken to avoid an excess of ammonium hydroxide.

[9] Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Max Drechsel, Bern.

In order to compare more exactly the effect of an excess of ammonium hydroxide the experiments labeled III were performed. These duplicated Procedure II except that after carefully neutralizing with ammonia an excess of 2 ml. of 6 normal solution was added.

In each of the experiments 250 milligrams of one of the elements listed in the first column of the table was precipitated from a solution which also contained 250 milligrams of one of the elements listed at the top of the four major columns. Observations and variations from the procedures outlined above are contained in the notes to the table. The precipitate was then analyzed in order to determine the amount of the soluble element carried down. Limitation of space has made it necessary to omit a detailed description of the methods used in analyzing these precipitates. In every case the precipitate was so treated as to separate the two elements—thus the ferric hydroxide precipitates were dissolved in hydrochloric acid, the concentration of the acid properly adjusted and the iron removed by repeated extraction with ether—or the element carried down was converted into a form in which it could be directly estimated; for example, the manganese in the aluminum precipitate was converted directly into manganese dioxide, or, when very small in amount, oxidized to permanganate. The methods used were checked by blanks and by confirmatory analyses of prepared mixtures. The results of these experiments, showing the amount of co-precipitation in each separation, have been collected in Table I. It is felt that significance should be attached to the general magnitude, rather than the exact value for any individual experiment, as it is impossible to duplicate exactly all the conditions, such as local concentration of the precipitant during precipitation, and as in many cases the results are apparently highly dependent upon such conditions.

TABLE I

THE SEPARATION OF CHROMIUM, ALUMINUM AND IRON FROM MANGANESE, NICKEL, COBALT AND ZINC BY PRECIPITATION WITH AMMONIA

In these experiments 250 mg. of one of the elements in the first column was precipitated from a solution containing 250 mg. of one of the elements listed at the top of the four major columns.

	Manganese				Nickel			
Element precipitated	Expt.	Procedure	Mn in ppt. mg.	Notes	Expt.	Procedure	Ni in ppt., mg.	Notes
Chromium	1	I	55	1	6	I	114	
	2	II	0.8		7	I	163	4
	3	II	0.4	2	8	I	150	5
	4	II	0.5	3	9	II	28	
	5	III	18	2	10	II	26–28	6
					11	III	35	
Aluminum	19	I	4.0		23	I	230	
	20	II	0.2		24	II	10	
	21	II	0.3		25	III	190	
	22	III	2.5					
Ferric iron	35	I	2.0		39	I	16	
	36	II	1.5		40	II	3–4	6
	37	II	0.8		41	III	8–10	6
	38	III	2.7		48	III	13	10,11
					49		13	10,11

TABLE I (*Concluded*)

Element precipitated	Cobalt				Zinc			
	Expt.	Procedure	Co in ppt., mb.	Notes	Expt.	Procedure	Zn in ppt., mg.	Notes
Chromium	12	I	160		16	I	212	
	13	II	34		17	II	41	
	14	II	61	7	18	III	165	
	15	III	90					
Aluminum	26	I	230		31	I	214	
	27	I	216		32	II	75	
	28	II	8		33	III	121	
	29	III	166		34	II	68	9
	30	I, II	23	8				
Ferric iron	42	I	16		45	I	106	
	43	II	4		46	II	11	
	44	III	8		47	III	27	
					50	III	21	10
					51		19	10

NOTES TO TABLE I

1. The manganese in this precipitate was separated by precipitation as dioxide by addition of potassium chlorate to a nitric acid solution. The precipitate was washed free of chromate and chlorate and the manganese determined iodometrically.

2. The chromium hydroxide precipitate obtained in Expt. 3 required about 100 ml. of wash solution. However, the precipitate in Expt. 5 required 500 ml. The washings were tested for manganese by addition of ammonia and hydrogen peroxide.

3. In this neutralization a slight excess of ammonia was added, so 6 normal hydrochloric acid was added until the methyl red was distinctly pink and the neutralization repeated.

4. A slightly larger excess of ammonia was added in Expts. 7 and 8 than in 6.

5. Five grams of ammonium chloride was used in addition to that formed by neutralization of the hydrochloric acid.

6. The nickel was estimated by comparing with standards the precipitate produced by dimethylglyoxime in one-tenth the filtrate.

7. The solution was made just neutral to litmus without using a reference solution with an internal indicator. Probably slightly more ammonia was added than in Expt. 13.

8. The volume and other conditions were as in Procedure I. Neutralization was made and an excess of ammonia avoided as in Procedure II.

9. Only 160 mg. of zinc was taken.

10. In Expts. 49 and 51 an excess of 5 ml. of 15 normal ammonia was added; otherwise Expts. 48 and 49 and Expts. 50 and 51 were carried out in exact duplicate to note the effect of the larger excess of ammonia.

11. Expts. 48 and 49 were carried out in this Laboratory by Mr. Francis Hunter and Mr. Elvin Lien.

Discussion of the Data of Table I

An inspection of the data in Table I would seem to lead to two general conclusions: first, in about half of the separations studied the separation is quite unsatisfactory even under the most favorable conditions. Second, in every case studied the separation is more effective when an

excess of ammonia is avoided and, in most cases, unless this excess is avoided the separation is so imperfect that little is gained by reprecipitations; thus, under the conditions studied, when an excess of ammonia is added, more than 50% of the nickel, cobalt or zinc is carried out by either chromium or aluminum. This would seem to indicate that the ammonia separation is more effectively carried out, at least in dilute solutions, as a process of selective hydrolysis and not as one depending on the formation of the soluble complex ammino ions. In support of this it is to be noted that manganese, where the tendency toward this complex formation is least, is much less co-precipitated than nickel, cobalt or zinc.

Also, the P_H values at which these divalent elements are precipitated from solution are given by Britton[10] as follows: zinc, 5.2; nickel, 6.7; cobalt, 6.8; and manganese, 8.5–8.8. It is seen that the co-precipitation in the experiments carried out by Procedure II in every case varies in amount in this same order—zinc, the least soluble hydroxide, showing the greatest tendency to be carried with the precipitate. The same order in general holds for the experiments by Procedures I and III, which is somewhat surprising, as, with an excess of ammonia present, it would be expected that the formation of the soluble ammonia complexes would be a more deciding factor; for the same reason it would have been predicted that the large excess of ammonia added in Expts. 49 and 51 would have decreased markedly the amount of co-precipitation; however, the difference is within the experimental variations. That the effect is due to an adsorption process and not to mechanical inclusion or local precipitation is indicated by the experiments of Ibbotson and Brearly[11] and of Noyes and Bray,[12] showing that when an ammoniacal solution of the bivalent element is added to a suspension of the freshly precipitated hydroxide, the effect approaches that obtained by precipitation in the presence of the bivalent element. That the complex ammonia compounds are not extensively carried down was shown by the fact that relatively little ammonia was found upon analyzing an aluminum precipitate, produced by Procedure III, which had co-precipitated with it about 200 mg. of nickel. Further studies are being made of certain of these separations in which the co-precipitation is pronounced in an attempt to ascertain the various factors affecting it and the mechanism of the phenomenon.

Specifically, in addition to confirming the results of Lundell and Knowles that, by proper methods of neutralization, a satisfactory separation of manganese from aluminum and from iron is obtained, it is shown that under these same conditions manganese can be separated from chromium. However, it is to be noted that the co-precipitation of manganese is in-

[10] Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1929, p. 254, 278.

[11] Ibbotson and Brearly, *Chem. News*, **81**, 193 (1900).

[12] Ref. 3, p. 154.

creased much more by an excess of ammonia in the separation from chromium than it is in the separation from either aluminum or iron. The separations of nickel from aluminum and chromium show from 50 to 90% of this element brought down when an excess of ammonia is added, demonstrating the futility of reprecipitations; the same general behavior is obtained with these elements and cobalt. Even under the most favorable conditions these separations are hardly adequate for quantitative work. The separations of nickel and cobalt from iron, made from carefully neutralized solutions, show about 2% co-precipitation so that a reprecipitation would probably reduce this to satisfactory limits. The separation of zinc under these conditions is unsatisfactory regardless of methods of neutralization. It is to be noted that the co-precipitation in method I is usually greater than that in method III, showing the favorable effect of an increased volume with thereby a decrease in the concentration of the co-precipitated substance.

It is perhaps worthy of note that the procedure, almost universal in qualitative textbooks, which directs that a *slight excess* of ammonia be added to a relatively small volume of solution, produces conditions which are apparently the *least* favorable of those studied for the separations desired.

The Ardagh Method of Carrying out the Ammonia Separation.—Recognizing the inadequate nature of the conventional ammonia precipitation for the separation of iron (and aluminum) from zinc, Ardagh and his co-workers[13,14] have devised a procedure for carrying out the separation which employs radically different conditions from those existing in any of the procedures thus far described. In it the precipitation is made by the addition of a large excess of 15 *N* ammonium hydroxide to a very small volume of an acid solution which has been previously saturated with solid ammonium chloride. These conditions produce a more compact and granular precipitate than that usually formed and a satisfactory separation of zinc from iron or aluminum is obtained by a single precipitation. An extension of this method to other separations would seem desirable and, since no such data seemed available, such a study was made and the results are shown in Table II. The general procedure used was as follows. A hydrochloric acid solution of the elements to be separated was evaporated to a volume of 3 to 5 ml., cooled and 5 g. of solid ammonium chloride then intimately mixed with the solution. Following this 10 ml. of 15 *N* ammonium hydroxide was added, the resulting mixture thoroughly mixed with a stirring rod, 25 ml. of water added and the precipitate filtered, usually equally dividing it between two separate filters in order to facilitate washing. The precipitates were washed with a solution containing 5 g. of ammonium chloride and 5 ml. of 15 *N* ammonium hydroxide in a volume of 100 ml.

[13] Ardagh and Broughall, *Can. Chem. Met.*, **7**, 198 (1923).

[14] Ardagh and Bongard, *Ind. Eng. Chem.*, **16**, 297 (1924).

Variations from this procedure are explained in the notes accompanying the table. It should be mentioned that chromium cannot be precipitated under the conditions of this procedure as it remains to a large extent in solution due to the formation of complex ammines. Also from 2–5 milligrams of aluminum is dissolved and has to be recovered subsequently from the filtrate.

In these experiments 250 milligrams of one of the elements listed in the first column of the table was taken together with 250 milligrams of one of the elements listed at the top of the four major columns. Observations and variations from the outlined procedure are contained in the notes to the table.

TABLE II

THE SEPARATION OF ALUMINUM AND IRON FROM MANGANESE, NICKEL, COBALT AND ZINC BY THE ARDAGH METHOD OF PRECIPITATION WITH AMMONIA

In each experiment 250 mg. of one of the elements in the first column was taken with 250 mg. of one of the elements listed at the top of the four main columns

Element precipitated	Manganese Found in ppt. Expt.	mg.	Notes	Nickel Found in ppt. Expt.	mg.,	Notes	Cobalt Found in ppt., Expt.	mg.	Notes	Zinc Found in ppt., Expt.	mg.	Notes
Aluminum	1	64	1	3	4	3	4	4	4	5	15	5, 8
	2	105	2							6	8	6, 8
										7	2	7, 8
											0–0.4	14
Iron	8	25		10	0.1–0.2		11	25	10	14	0.5	12
	9	8	9	16	0.7–0.9	13	12	5	10	15	0.6	13
							13	6	11		0.2–0.5	14

NOTES TO TABLE II

1. The precipitate was equally divided between two filters and each half required 150–200 ml. of wash solution; it darkened during the washing.
2. Only 5 cc. of 15 *N* ammonium hydroxide was used.
3. Found 5 mg. of aluminum in the filtrate.
4. Filtration and washing difficult; 200 ml. wash solution required.
5. Only 2 ml. of 15 *N* ammonium hydroxide was added and the mixture was diluted to 50 ml. before filtering. Less than 0.5 mg. of aluminum remained in the filtrate.
6. Only 3 ml. of ammonia added, mixture diluted to 25 ml. 1–2 mg. of aluminum found in filtrate.
7. Only 5 ml. ammonia added. 2–3 mg. of aluminum in filtrate.
8. In Expts. 5, 6, 7 only 125 mg. of aluminum was taken with 250 mg. of zinc.
9. Only 5 ml. of ammonia added.
10. In this experiment (No. 11) the original solution was evaporated to 3–4 ml. and this solidified upon cooling. Two ml. of 6 *N* hydrochloric acid was added to dissolve this residue. Upon adding the ammonium chloride this solution was absorbed and even after long maceration with a stirring rod the mixture did not seem homogeneous. In Expt. 12 the original solution was evaporated to 5 ml. and after adding the ammonium chloride, 6 *N* hydrochloric acid was added (2 cc.) until a homogeneous, thoroughly wet mixture was obtained.
11. A repetition of Expt. 12, except that the mixture was heated to 70–80° before filtering and the wash solution was also heated. The precipitate was more difficult to wash, requiring 500 ml. of wash solution.

12. 5 g. of ammonium nitrate was used instead of ammonium chloride.

13. A nitric acid solution was evaporated to 3–4 ml. and 8 g. of ammonium nitrate used instead of the ammonium chloride. Ammonium nitrate was substituted for ammonium chloride in the wash solution.

14. Values taken from experiments of Ardagh and Bongard[14] using about 200 mg. of iron and zinc.

Discussion of the Data of Table II

An inspection of the data of Table II, and a comparison with Table I, shows, as was to be expected, that the Ardagh method cannot be used for separations involving manganese, due to the oxidation of this element in the more alkaline solution. The separation of nickel from aluminum is improved and the separation of nickel from iron is so nearly perfect that only one precipitation would be required for most quantitative work. The separation of cobalt from aluminum is more complete than by any method of precipitation by ammonia in a dilute solution; although the separation of cobalt from iron is fairly satisfactory it is no more complete than that obtained by a careful neutralization. Where, as is the case in many qualitative systems, it is desired to separate iron from nickel, cobalt and zinc, the Ardagh method of precipitation offers decided advantages.

Attempts to reduce the amount of aluminum dissolved by decreasing the ammonia concentration caused, in the separation from zinc, an increase in the co-precipitation of that element (Expts. 5, 6, 7). This indicates that in this separation, contrary to those studied in Table I, the bivalent elements are held in solution mainly due to the formation of the ammonia complexes. That, in spite of the use of small volumes and more concentrated solutions, better separations are obtained by this method, is probably due to this more complete conversion of the bivalent elements into the ammonia complexes and, in addition, to the more granular and less hydrous nature of the precipitates obtained, these physical characteristics usually indicating a less effective adsorbing agent.[15] Experiments 14, 15 and 16 show that the substitution, in the cases studied, of an equivalent amount of ammonium nitrate for ammonium chloride has relatively little effect, indicating that the presence of chloride ion is not highly essential to the separation.

The Separation of Bismuth from Copper and Cadmium

In most systems of qualitative analysis this separation follows the detection and removal of lead as sulfate. In precipitating lead the solution is fumed with sulfuric acid, then cooled and diluted. To conform to these conditions the procedure used was as follows: to 250 mg. each of bismuth and of copper or cadmium (as the nitrates), was added 10 ml. of 6 *N* sulfuric acid and the volume made from 80–100 ml. There was then added

[15] Weiser, "The Hydrous Oxides," The McGraw-Hill Book Co., New York, 1926, p. 1.

6 *N* ammonia until in one case the solution was just neutral to litmus or, in the alternative case, there was 5 ml. of ammonia in excess. The precipitates were washed with 2% ammonium sulfate solution and then analyzed for the copper and cadmium present. In the separations in which the solution was made just neutral and an excess of ammonia was avoided, 150–180 mg. of copper and 2 mg. of cadmium were found in the bismuth precipitates; in the separations with the 5 ml. excess of ammonia added 0.5 mg. of copper and 2 mg. of cadmium were found. This indicates, as would be expected from the P_H value at which copper precipitates, that the separation of copper from bismuth in a sulfate solution requires an excess of ammonia sufficient to form the complex ammine; on the other hand, the separation of cadmium, due to the greater solubility of the hydroxide, is equally effective with or without an excess of ammonia.

Summary

Data are presented for the separation of chromium, aluminum and iron from manganese, nickel, cobalt and zinc by various modifications of the ammonia separation.

It is shown that when working with the usual dilute solutions the separation is more effective when a careful neutralization is made using methyl red (or its equivalent) as indicator, and an excess of ammonia avoided. Under these conditions, with 250 mg. of each element present, the chromium precipitate carried out only 0.4–0.8 mg. of manganese, but 30–40 mg. of nickel, cobalt or zinc; the aluminum precipitate carried out only 0.2–0.3 mg. of manganese, but 8–10 mg. of nickel or cobalt and 75 mg. of zinc; the iron precipitate carried out 0.8–1.5 mg. of manganese, 3–4 mg. of cobalt or nickel and 11 mg. of zinc.

When an excess of ammonia is used the separation is so imperfect, regardless of the presence of a large amount of ammonium chloride, that in the majority of cases it is not recommended even for qualitative purposes.

When the precipitation is made by addition of concentrated ammonium hydroxide to a small volume (3–5 ml.) of a solution saturated with ammonium chloride, even with 250 mg. of each element present, less than a milligram of the soluble element was co-precipitated in separating iron from nickel or zinc, or aluminum from zinc, and 4–5 mg. was co-precipitated in separating iron from cobalt, or aluminum from nickel or cobalt. Under the conditions of the procedure aluminum dissolves to the extent of about 5 mg., and chromium is very soluble.

When separating bismuth from copper in a dilute sulfate solution an excess of ammonia is required; the separation from cadmium can be made either from a carefully neutralized solution or one containing an excess of ammonia.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

EQUILIBRIUM IN BINARY SYSTEMS UNDER PRESSURE. II. THE SYSTEM, K_2SO_4–H_2O, AT 25°

BY L. H. ADAMS

RECEIVED JANUARY 7, 1932 PUBLISHED JUNE 6, 1932

In a previous paper[1] the results of an investigation of the system, NaCl–H_2O, under high pressures were presented. Measurements of the effect of hydrostatic pressure on the volumes of the several phases were made, and thence, by the application of a simple thermodynamic principle, the conditions of equilibrium between the various phases were calculated for pressures somewhat greater than 10,000 bars (metric atmospheres). The freezing-point and solubility curves thus delineated were confirmed by direct measurements, but the indirect, *i. e.*, thermodynamic, method was the one that was found to be the most convenient for the study of multicomponent systems under high pressure.

In this paper are given results for the system, K_2SO_4–H_2O, at 25° and at pressures up to approximately 10,000 bars. The experimental and calculatory methods were essentially the same as those used in the previous investigation, and the nomenclature, except where the contrary is specifically noted, is the same as that of the former paper.

Measurements of the Compression of the Solutions

Low-Pressure Experiments.—Since the high-pressure apparatus is not suitable for measurements at pressures below 1000 bars, the compression at this pressure was determined by means of the glass piezometer previously described.[2] The solutions were made up by weight from potassium sulfate that had been recrystallized from water and dried at about 800°. On account of the transition with large volume change, which potassium sulfate undergoes at 588°, heating the salt above this temperature not only insures thorough drying but also reduces the crystals to a convenient granular condition.

The most concentrated solution used contained 10% by weight, since the solubility of potassium sulfate at 25° and atmospheric pressure is only 10.76%. Table I shows the results for the compression, k (fractional diminution in volume), at 1000 bars for solutions of four different concentrations, and the previously determined value of k for pure water. The weight fraction of salt is denoted by x_2. In Table I are given also the values of the important compression–concentration gradient, $\partial k/\partial x_2$, and the values of $\bar{v}_1$ and $\bar{v}_2$, the fictive volumes of water and potassium sulfate at 1000 bars, or rather the change in these quantities caused by the pressure

[1] L. H. Adams, THIS JOURNAL, **53**, 3769–3813 (1931).

[2] Adams, Ref. 1, p. 3774.

TABLE I

COMPRESSION, k, OF POTASSIUM SULFATE SOLUTIONS AT 1000 BARS AND 25°

x_2	k	$-\partial k/\partial x_2$	$\bar{v}_1 - (\bar{v}_1)_0$	$\bar{v}_2 - (\bar{v}_2)_0$
0.0	0.03930	0.0640	−0.0394	0.0568
.025	.03787	.0624	− .0393	.0513
.05	.03647	.0608	− .0392	.0470
.075	.03470	.0592	− .0389	.0429
.10	.03322	.0576	− .0385	.0391

mentioned. The values of $\partial k/\partial x_2$ were obtained by differentiating the equation

$$k = 0.03930 - 0.0640\, x_2 + 0.032\, x_2^2 \qquad (1)$$

which, over the limited concentration range obtainable with this salt, seemed to give a fair representation of the data except possibly at concentrations very close to zero. The values of $\bar{v}_1$ and $\bar{v}_2$ were obtained from the relations [equations (29) and (28), respectively, of the previous paper]

$$\bar{v}_1 - (\bar{v}_1)_0 = -(\bar{v}_1)_0\, k + x_2 v_0 \frac{\partial k}{\partial x_2} \qquad (2a)$$

and

$$\bar{v}_2 - (\bar{v}_2)_0 = -(\bar{v}_2)_0\, k - x_1 v_0 \frac{\partial k}{\partial x_2} \qquad (2b)$$

in which v is the specific volume of the solution, and the subscript zero refers to atmospheric pressure.

High-Pressure Experiments.—For pressures above 1000 bars the measurements of the compression, k, were made by the usual piston-displacement method. The directly determined quantity was the difference between the compression of the solution (reckoned from 2000 bars, the arbitrary "initial" pressure) and that of pure water, that is, $\Delta k - \Delta k'$, the superscript prime referring to $P = 2000$. The results are shown in Table II, which includes also the values of k itself for the various concentra-

TABLE II

COMPRESSION, k, OF POTASSIUM SULFATE SOLUTIONS AT HIGH PRESSURES

P, bars	$-10^5(\Delta k - \Delta k')$ $x_2 = 0$	k	$-10^5(\Delta k - \Delta k')$ $x_2 = 0.025$	k	$-10^5(\Delta k - \Delta k')$ $x_2 = 0.05$	k	$-10^5(\Delta k - \Delta k')$ $x_2 = 0.075$	k	$-10^5(\Delta k - \Delta k')$ $x_2 = 0.10$	k
1	0	0.0000		0.0000		0.0000		0.0000		0.0000
1000	0	.0393	− 85	.0378	−212	.0365	−276	.0347	− 380	.0332
2000	0	.0699	0	.0675	0	.0650	0	.0625	0	.0600
3000	0	.0945	73	.0914	128	.0883	177	.0854	250	.0821
4000	0	.1152	130	.1115	226	.1080	326	.1046	472	.1006
5000	0	.1330	184	.1288	311	.1250	425	.1214	618	.1169
6000	0	.1485	222	.1439	340	.1402	504	.1361	724	.1314
7000	0	.1622	191	.1579	366	.1536	543	.1494	811	.1442
8000	0	.1746	226	.1700	415	.1655	627	.1610	922	.1555
9000	0	.1858	215	.1813	425	.1766	632	.1721	934	.1666
10000	0	.1964	221	.1918	425	.1872	661	.1824	1003	.1765

tions and pressures, as obtained by combining[3] the results for $\Delta k - \Delta k'$ with those for Δk at 1000 bars given in Table I and with the previously determined values for the compression of water. A comparison of the compression of solutions of potassium sulfate with the previous results for sodium chloride shows that the addition of a given *weight* of potassium sulfate reduces the compression of water (at any pressure) almost the same amount as the addition of the same weight of sodium chloride, although the latter salt produces a slightly greater effect.

Density of Potassium Sulfate Solutions.—Before use can be made of these measurements for determining the equilibrium in the system, K_2SO_4–H_2O, it is necessary to have reliable data on the densities of the solutions at atmospheric pressure. These densities should be known to about one unit in the fifth place after the decimal point in order to obtain the desired accuracy in the fictive volumes of the two components. Unfortunately, there are only a few salts for which the densities of their aqueous solutions have been measured with reasonable accuracy—despite the fact that the determination of density is one of the simplest and the most fundamental of measurements. The best values for potassium sulfate solutions (as shown in the "International Critical Tables") are given only to the fourth figure after the decimal, and, as has now been found, there are errors as great as eight units in this place. It was necessary, therefore, to make a series of measurements on the densities of the solutions at 25°. This was done, with the recrystallized and carefully dried salt, according to the same method and by the use of the same pycnometer as that described in connection with earlier density determinations at this Laboratory.[4] The temperature of the thermostat was 25° ± 0.003 and the volume of the pycnometer at 25° was 55.0373 ml. This volume agreed well with the previous determinations, *viz.*, 55.0384 (Hall, 1920), 55.0365 (Gibson, 1927), and 55.0371 (Gibson, 1930).

The results are shown in Table III, and the "densities," d, in ml./g. and the "specific volumes," v, in g./ml. at round concentrations are given in Table IV. It was noted that for potassium sulfate, and also for other salts, $\Delta v/\Delta x_2$ when plotted against x_2 gave a line which curved notably at the origin but with increasing concentration rapidly approached a straight line. This at once suggested that the data might be represented well by an equation of the form

$$v = A + Bx_2 + Cx_2^2 + D(1 - e^{-Ex_2}) \qquad (3)$$

in which A, B, C, D and E are constants, A being the specific volume of pure water (1.002932 at 25°). It was found that with $B = 0.79032$, $C = 0.297$, $D = 2.40 \times 10^{-4}$ and $E = 100$, this equation represented the

[3] Adams, Ref. 1, p. 3782.

[4] R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 167–173 (1924); R. E. Gibson, *J. Phys. Chem.*, **31**, 496–510 (1927); *ibid.*, **35**, 690–699 (1931).

TABLE III

DENSITIES AND SPECIFIC VOLUMES OF POTASSIUM SULFATE SOLUTIONS AT 25°

x_2	d, g./ml.	$v_{obs.}$, ml./g.	$v_{calcd.}$	Diff. × 10^6 (obs. − calcd.)
0.0000	0.997077	1.002932	1.002932	0
.4995	1.001101	0.998900	0.998897	3
.5001	1.001112	.998889	.998892	−3
2.5012	1.017154	.983135	.983131	4
4.9939	1.037375	.963972	.963967	5
5.0011	1.037426	.963924	.963913	11
7.5033	1.058132	.945062	.945064	−2
9.8655	1.078029	.927619	.927613	6
10.0038	1.079214	.926600	.926602	−2

TABLE IV

SPECIFIC VOLUMES OF POTASSIUM SULFATE SOLUTIONS AT ROUND CONCENTRATIONS, AND THE FICTIVE VOLUMES OF THE TWO COMPONENTS. TEMPERATURE, 25°

x_2	v, ml./g.	d, g./ml.	$\bar{v}_1$	$\bar{v}_2$
0.000	1.002932	0.997077	1.00293	0.183
.025	$.983140$	1.017149	1.00258	.2252
.050	$.963921$	1.037430	1.00196	.2411
.075	$.945089$	1.058102	1.00102	.2553
.100	$.926630$	1.079179	0.99972	.2688

data with gratifying accuracy. As indicated by the last column of Table III, the average deviation (without regard to sign) between the observed values of v and those calculated from equation (3) was only 4×10^{-6}, which was no greater than the error of measurement.

The fictive volumes, $\bar{v}_1$ and $\bar{v}_2$, of water and potassium sulfate in solution were calculated from the equations

$$\bar{v}_1 = v - x_2 \frac{dv}{dx_2} \tag{4a}$$

and

$$\bar{v}_2 = v + x_1 \frac{dv}{dx_2} \tag{4b}$$

the values of dv/dx_2 being obtained by differentiating equation (3); except that, because there was good reason for believing that equation (3), despite the satisfactory way in which it fits the data, does not give precisely the right slope at *zero* concentration, the value of $\bar{v}_2$ at $x_2 = 0$ was determined by plotting the values of $\bar{v}_2$ against $\sqrt{x_1/x_2}$ and extrapolating the (nearly linear) curve back to zero. The results for $\bar{v}_1$ and $\bar{v}_2$ are shown in Table IV.

Fictive Volumes under Pressure.—The change of the fictive volumes under pressure is determined by the compression, k, of the solutions. The most convenient method of carrying out the calculation depends on the ease with which k can be represented as a function of x_2 (at constant P) or of P (at constant x_2). With potassium sulfate solutions, just as was

found previously for sodium chloride solutions, the compression reckoned from 2000 bars (that is, $k-k'$) seems to vary linearly with the concentration at constant pressure. Hence it was advantageous to deal directly with $k-k'$ and to calculate the increase in $\bar{v}_1$ and $\bar{v}_2$, respectively, due to an increase of pressure from 2000 to P, by the relations

$$\bar{v}_1 - \bar{v}_1' = -(\bar{v}_1)_0(k - k') + x_2 v_0 \frac{\partial(k - k')}{\partial x_2} \qquad (5a)$$

and

$$v_2 - \bar{v}_2' = -(v_2)_0(k - k') - x_1 v_0 \frac{\partial(k - k')}{\partial x_2} \qquad (5b)$$

The first step consisted in finding $\partial(k-k')/\partial x_2$ at each pressure. This was done by representing $k-k'$ as a linear function of x_2 using the method of least squares. Next, the values of this compression–concentration gradient were smoothed by means of the equation

$$-10^5 \frac{\partial(k - k')}{\partial x_2} = 0.304(P - P') + 8000\,(1 - e^{-3.4 \times 10^{-4}(P - P')}) \qquad (6)$$

which fitted the results for the gradient with an average deviation (regardless of sign) of 0.0014. Then, $\bar{v}_1 - \bar{v}_1'$ and $\bar{v}_2 - \bar{v}_2'$ at each pressure from 1000 to 10,000 bars were computed by means of equations (5a) and (5b); and finally, by use of the change in $\bar{v}_1$ and in $\bar{v}_2$ from 1 to 1000 bars, as shown in Table I, the values of $\bar{v}_1$ and $\bar{v}_2$ at the various pressures were obtained.

The fictive volumes under pressure were calculated also by another method, suggested by the recent discovery[5] that the "apparent molal volume" of electrolytes is a linear function of the square root of the concentration per unit volume for dilute solutions, and is very approximately so for concentrated solutions. The approximate linear relation holds also if the mole ratio or the mass ratio is substituted for the volume concentration. If φ be defined[6] by the relation, $\varphi = v/x_2 - x_1 v_w/x_2$, in which v_w is the specific volume of pure water, and if φ is a linear function of $\sqrt{x_2/x_1}$ not only at atmospheric pressure but also at all other pressures, then it follows that

$$\Delta_P\varphi \equiv \frac{\Delta_P v - x_1 \Delta_P v_w}{x_2} = a + b\left(\frac{x_2}{x_1}\right)^{1/2} \qquad (7)$$

in which a and b are constants (for a given salt and at a given temperature and pressure). Furthermore, from equation (7) in combination with

[5] D. O. Masson, *Phil. Mag.*, [7] **8**, 218–235 (1931); A. F. Scott, *J. Phys. Chem.*, **35**, 2315–2319 (1931); W. Geffcken, *Z. physik. Chem.*, **155A**, 1–28 (1931). See also the accurate measurements by A. B. Lamb and R. E. Lee [THIS JOURNAL, **35**, 1666–1693 (1913)] on the densities of very dilute aqueous salt solutions. From a study of these results it may be seen that the square root plot for moderate concentration may be extrapolated with safety to zero, or at least to extremely small concentrations.

[6] It should be noted that here φ is not the "apparent molal volume" (as usually defined); it is that quantity divided by the formula weight of the salt, and might be called the "apparent specific volume" of the salt in solution.

equations [similar to (4a) and (4b)] for the fictive volumes under pressure in terms of Δv, it may readily be shown that

$$\Delta_P \bar{v}_1 \equiv \bar{v}_1 - (\bar{v}_1)_0 = \Delta_P v_w - \frac{b}{2}\left(\frac{x_2}{x_1}\right)^{3/2} \tag{8a}$$

and

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = a + \frac{3b}{2}\left(\frac{x_2}{x_1}\right)^{1/2} \tag{8b}$$

The supposition that (7) would give a faithful representation of the compression results was confirmed by applying the equation to the previously obtained data for sodium chloride solutions.

In order to calculate $\bar{v}_1$ and $\bar{v}_2$ under pressure by these equations, the values of k for the potassium sulfate solutions, as given in Table II, were converted to Δv's by the relation, $\Delta_P v = -v_0 k$, then $\Delta_P \varphi$ was calculated, and a and b at each pressure determined graphically by plotting $\Delta_P \varphi$ against $\sqrt{x_2/x_1}$. These values of a and b were then used in equations (8a) and (8b) to calculate $\bar{v}_1$ and $\bar{v}_2$ at the various pressures. The fictive volumes thus calculated agreed well with those calculated by the previous method,

TABLE V

FICTIVE VOLUME OF WATER IN POTASSIUM SULFATE SOLUTIONS UNDER PRESSURE

Pressure in bars	$\bar{v}_1$ $x_2 = 0$	$10^4\Delta x\bar{v}_1$	$\bar{v}_1$ $x_2 = 0.025$	$10^4\Delta x\bar{v}_1$	$\bar{v}_1$ $x_2 = 0.05$	$10^4\Delta x\bar{v}_1$	$\bar{v}_1$ $x_2 = 0.075$	$10^4\Delta x\bar{v}_1$	$\bar{v}_1$ $x_2 = 0.10$	$10^4\Delta x\bar{v}_1$
1	1.0029	0	1.0026	−3	1.0020	−9	1.0010	−19	0.9997	−32
1000	0.9635	0	0.9633	−2	0.9628	−7	0.9621	−14	.9612	−23
2000	.9328	0	.9327	−1	.9322	−6	.9317	−11	.9309	−19
3000	.9081	0	.9080	−1	.9076	−5	.9072	− 9	.9065	−16
4000	.8874	0	.8873	−1	.8869	−5	.8865	− 9	.8860	−14
5000	.8695	0	.8694	−1	.8691	−4	.8687	− 8	.8682	−13
6000	.8540	0	.8539	−1	.8534	−4	.8533	− 7	.8529	−11
7000	.8402	0	.8402	0	.8398	−4	.8396	− 6	.8392	−10
8000	.8278	0	.8278	0	.8275	−3	.8273	− 5	.8269	− 9
9000	.8166	0	.8166	0	.8163	−3	.8161	− 5	.8157	− 9
10000	.8059	0	.8059	0	.8057	−2	.8055	− 4	.8051	− 8

TABLE VI

FICTIVE VOLUME OF POTASSIUM SULFATE IN AQUEOUS SOLUTIONS UNDER PRESSURE

Pressure in bars	$\bar{v}_2$ $x_2 = 0$	$10^3\Delta x\bar{v}_2$	$\bar{v}_2$ $x_2 = 0.025$	$10^3\Delta x\bar{v}_2$	$\bar{v}_2$ $x_2 = 0.05$	$10^3\Delta x\bar{v}_2$	$\bar{v}_2$ $x_2 = 0.075$	$10^3\Delta x\bar{v}_2$	$\bar{v}_2$ $x_2 = 0.10$	$10^3\Delta x\bar{v}_2$
1	0.183	0	0.225	42	0.241	58	0.255	72	0.269	86
1000	.243	0	.277	34	.288	45	.298	55	.308	65
2000	.279	0	.306	27	.316	37	.324	45	.332	53
3000	.302	0	.326	24	.334	32	.341	39	.348	46
4000	.318	0	.340	22	.347	29	.354	36	.360	42
5000	.329	0	.350	21	.357	28	.362	33	.367	38
6000	.338	0	.358	20	.364	26	.368	30	.373	35
7000	.345	0	.363	18	.369	24	.373	28	.377	32
8000	.350	0	.367	17	.372	22	.376	26	.380	30
9000	.354	0	.371	17	.375	21	.379	25	.382	28
10000	.357	0	.373	16	.377	20	.380	23	.384	27

except for $\bar{v}_2$ at $x_2 = 0$. It seems probable that equation (7) takes account of the peculiar relations in very dilute solutions of electrolytes much better than the previous method; therefore, for $\bar{v}_2$ at $x_2 = 0$ only the values obtained from (8b) are here recorded. The final results are given in Tables V and VI, which include also the values of $\Delta_x\bar{v}_1$ (the change with concentration, of $\bar{v}_1$ at a given constant pressure), and of $\Delta_x\bar{v}_2$.

Figure 1 is a graphical representation of the way in which pressure affects the fictive volume, $\bar{v}_2$, of potassium sulfate in aqueous solution. With increasing pressure, $\bar{v}_2$ for each concentration *increases*. In other words, the fictive compressibility is negative. This is similar to what was previously observed for sodium chloride in water. In the present case, however, no maximum is seen when $\bar{v}_2$ is plotted against P. This is probably because a maximum is more readily attained only at high concentrations, and the solubility of potassium sulfate is not large enough for the maximum to appear unless the pressure were appreciably higher than 10,000 bars, in which event (at 25°) the solution would freeze.

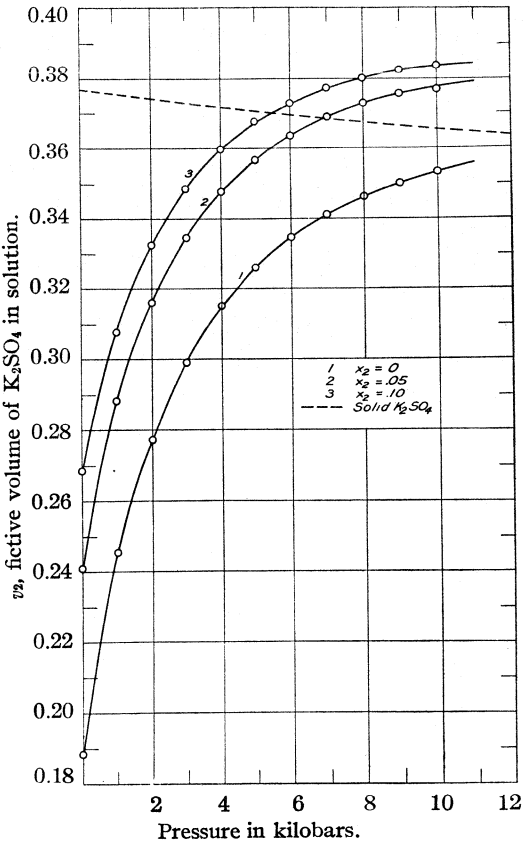


Fig. 1.—The effect of pressure on the fictive volume, $\bar{v}_2$, of potassium sulfate in aqueous solutions. Pressure produces a notable increase in $\bar{v}_2$, especially in dilute solutions. The dotted line shows the volume of solid K_2SO_4 at various pressures.

A plot of $\bar{v}_2$ or $\bar{v}_1$ against x_2 (at constant P) would again demonstrate the striking fact that under high pressure, solutions tend to become more simple in nature, that is, more nearly "normal." At atmospheric pressure the change of $\bar{v}_1$ or $\bar{v}_2$ with varying concentration is large for salts such as potassium sulfate, but at 10,000 bars both $\bar{v}_1$ and $\bar{v}_2$ are much less affected by changes in concentration, and the solutions thus behave more nearly like ideal solutions.[7]

[7] *Cf.* Adams, Ref. 1, p. 3795.

Determination of Equilibrium by the Thermodynamic Method

Calculation of μ_1 and μ_2.—Equilibrium between the various phases in a system is always in accord with the principle, enunciated by Gibbs, that for any actual component its chemical potential, μ, shall have at equilibrium the same value in all of the phases. The μ's may be readily calculated from the fictive volumes when these are known. As previously explained,[8] the most convenient method, in actual practice, is to use the equation

$$(x_1 \text{ constant}) \quad \Delta_x\mu_1 \equiv \mu_1 - (\mu_1)_w = \Delta_x(\mu_1)_0 + \int_1^P \Delta_x\bar{v}_1 dP \qquad (9)$$

for μ_1, and the similar equation for μ_2. As before, the subscript zero refers to atmospheric pressure and the subscript w to pure water (zero concentration).

In Table VII are shown the results of the calculation concerning μ_1. Under each concentration are two columns; the first gives $\Delta_x/(\mu_1)_0 - \Delta_x\mu_1$, that is, the negative of the definite integral in equation (7), and the second gives $-\Delta_x\mu_1$, obtained by subtracting the value of $\Delta_x(\mu_1)_0$ (at that concentration) from the values in the first column.

TABLE VII

CHEMICAL POTENTIAL, μ_1, OF WATER IN POTASSIUM SULFATE SOLUTIONS UNDER PRESSURE

$\Delta_x\mu_1$ is the difference (in joules) between the value of μ_1 for the particular concentration and the value for pure water at the same pressure.

Pressure in bars	$(\Delta_x\mu_1)_0 - \Delta_x\mu_1$	$-\Delta_x\mu_1$	$(\Delta_x\mu_1)_0 - \Delta_x\mu_1$	$-\Delta_x\mu_1$	$(\Delta_x\mu_1)_0 - \Delta_x\mu_1$	$-\Delta_x\mu_1$	$(\Delta_x\mu_1)_0 - \Delta_x\mu_1$	$-\Delta_x\mu_1$	$(\Delta_x\mu_1)_0 - \Delta_x\mu_1$	$-\Delta_x\mu_1$
	$x_2 = 0$		$x_2 = 0.025$		$x_2 = 0.05$		$x_2 = 0.075$		$x_2 = 0.10$	
1	0	0	0.00	0.82	0.00	1.59	0.00	2.40	0.00	3.23
1000	0	0	.03	.85	.08	1.67	.16	2.56	.26	3.49
2000	0	0	.05	.87	.15	1.74	.28	2.68	.47	3.70
3000	0	0	.06	.88	.21	1.80	.38	1.78	.64	3.87
4000	0	0	.07	.89	.26	1.85	.47	2.87	.79	4.02
5000	0	0	.08	.90	.30	1.89	.55	2.95	.93	4.16
6000	0	0	.09	.91	.34	1.93	.63	3.03	1.05	4.28
7000	0	0	.09	.91	.38	1.97	.70	3.10	1.15	4.38
8000	0	0	.09	.91	.41	2.00	.76	3.16	1.25	4.48
9000	0	0	.09	.91	.44	2.03	.81	3.21	1.34	4.57
10000	0	0	.09	.91	.46	2.05	.85	3.25	1.42	4.65

The values of $\Delta_x(\mu_1)_0$, that is, $\mu_1 - (\mu_1)_w$ at atmospheric pressure, were obtained from data on the freezing points and vapor pressures of potassium sulfate solutions given in the "International Critical Tables" and from Åkerlöf's[9] measurements on the e. m. f. of cells containing potassium sulfate solutions, the method of calculation being the same as that described in the previous paper. The weighted mean of $\Delta_x(\mu_1)_0$ computed from the various kinds of data is shown in the first row of Table VII opposite $P = 1$.

[8] Adams, Ref. 1, p. 3798.

[9] G. Åkerlöf, THIS JOURNAL, **48**, 1160–1176 (1926).

Table VIII similarly gives the results of the calculation concerning the effect of pressure on μ_2. In this instance only $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$ is shown, and

TABLE VIII

EFFECT OF HIGH PRESSURE ON THE CHEMICAL POTENTIAL OF POTASSIUM SULFATE IN AQUEOUS SOLUTIONS

$\Delta_x\mu_2 - (\Delta_x\mu_2)_0$ is equivalent to $\Delta_P\mu_2 - (\Delta_P\mu_2)_w$. Here $\Delta_x\mu_2$ is the difference between the value of μ_2 for the particular concentration and the value at zero concentration and the same pressure.

Pressure in bars	$\Delta_x\mu_2 - (\Delta_x\mu_2)_0$ in joules				
	$x_2 = 0$	$x_2 = 0.025$	$x_2 = 0.05$	$x_2 = 0.075$	$x_2 = 0.10$
1	0	0.0	0.0	0.0	0.0
1000	0	3.7	5.1	6.3	7.5
2000	0	6.8	9.2	11.3	13.4
3000	0	9.3	12.6	15.5	18.3
4000	0	11.5	15.7	19.2	22.7
5000	0	13.7	18.5	22.7	26.7
6000	0	15.7	21.2	25.8	30.4
7000	0	17.5	23.7	28.7	33.7
8000	0	19.3	26.0	31.4	36.8
9000	0	21.0	28.2	34.0	39.7
10000	0	22.6	30.2	36.4	42.5

here $\Delta_x\mu_2$ means $\mu_2 - (\mu_2)_w$, not as in the first paper, $\mu_2 - (\mu_2)_s$, the subscript s referring to a fixed and arbitrary concentration. However, the values of $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$ given in Table VIII may by simple subtraction be transformed into the corresponding values on the former basis. It is important to remember that, although $\Delta_x\mu_2$ as now defined is always negatively infinite, this does not prevent its change with pressure, $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$, from having a finite value.[10]

The Freezing Pressure Curve of Ice$_{VI}$.—At 25° pure water freezes to ice$_{VI}$ at 9630 bars, but upon the addition of potassium sulfate (or almost any other solute) the freezing pressure is raised, by an amount determined by the equality of the μ's of ice$_{VI}$ and the water in solution at the given pressure. For convenience the consequent identity of $\mu_1 - (\mu_1)_w$ (*i. e.*, $\Delta_x\mu_1$) and $\mu_{VI} - (\mu_1)_w$ is utilized in the calculation of the freezing pressure curve. The values of the latter quantity[11] were taken from the previous paper. In order to find the freezing pressures at several concentrations, the values of $\Delta_x\mu_1$ for each concentration were plotted against pressure, and the intersections of these curves with the curve for $\mu_{VI} - (\mu_1)_w$ were then the freezing pressures at the respective concentrations. The results are shown in Table IX, which also gives for comparison the lowering of freezing temperature (of ice$_I$) at atmospheric pressure and at the same concentration. As in the case of sodium chloride and water, the freezing pressure curve shows a greater curvature than that of the freezing temperature.

[10] It may be useful to note that $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$ is identical with $\Delta_P\mu_2 - \Delta_P(\mu_2)_w$.

[11] Adams, Ref. 1, last column of Table X, p 3802.

It is interesting to calculate the theoretical initial slope of the freezing pressure curve. In general, for the change of freezing pressure

$$\frac{dP}{dx_2} = \frac{\partial\mu_1/\partial x_2}{v_{VI} - \bar{v}_1} \tag{10}$$

by analogy with the equation for the change of solubility under pressure.[12] By substitution of the value of $\partial\mu_1/\partial x_2$, as given by Gibbs' approximation for dilute solutions,[13] there is obtained

$$\frac{dP}{dx_2} = \frac{RT}{x_1^2 M_2'(\bar{v}_1 - v_{VI})} \tag{11}$$

for the slope at high dilutions. Taking $x_1 = 1$, $\bar{v}_2 - v_{VI} = 0.071$, $T = 298$, $R = 83$ decijoules, and $M_2' = 174.2/3 = 58.1$, we find dP/dx_2 at $x_2 = 0$ to be 60 bars for 1% change in salt concentration, which is slightly greater than the average slope from 0 to 2.5% as shown in the third column of Table IX.

TABLE IX

FREEZING PRESSURES OF ICE$_{VI}$ IN CONTACT WITH POTASSIUM SULFATE SOLUTIONS AT 25°

x_2, wt. fraction of K_2SO_4	P in bars	$P - P_0$ (ice$_{VI}$)	$t_0 - t$ (ice$_I$)	$10^2 \frac{t_0 - t}{P - P_0}$
0.0	9630	0	0.000	..
.025	9770	140	0.615	0.44
.05	9930	300	1.168	.39
.075	10100	470	1.742	.37
.10	10290	660		

For the initial slope of the freezing temperature curve we have the relation, similar to equation (11)

$$\frac{dT}{dx_2} = -\frac{RT^2}{x_1^2 M_2' \Delta\bar{h}_1} \tag{12}$$

in which $\Delta\bar{h}_1$ is approximately the heat of melting of ice$_I$ per gram. Combining equations (11) and (12) we obtain

$$\frac{(-dT/dx_2)_I}{(dP/dx_2)_{VI}} = \frac{T_I^2(\bar{v}_1 - v_{VI})}{T_{VI}\Delta\bar{h}_1} \tag{13}$$

which is an important relation for determining the limiting ratio, in dilute solution, between the freezing temperature lowering and the freezing pressure elevation. (This equation closely resembles the Braun equation for the relation between the effect of pressure and of temperature on solubility.) This limiting ratio is independent of the nature of the solute, and

[12] Adams, Ref. 1, equation (45), p. 3804.

[13] This may be written $\partial\mu_1/\partial x_2 = -RT/x_1^2 M_2'$. See R. W. Goranson, "Thermodynamic Relations in Multi-component Systems," Carnegie Institution of Washington, Publ. No. 408, 1930, p. 320. In general M_2' is the effective molecular weight of the solute, *i. e.*, one-third of the formula weight for a tri-ionic salt such as potassium sulfate in very dilute solutions.

depends only on the solvent; for water (if T_{VI} is 298°) it is 0.53×10^{-2}, which is in accord with the trend of the ratio given in the last column of Table IX.

The Solubility Curve of Potassium Sulfate.—The solubility at various pressures was calculated by means of the equation, used in the former paper

$$x_2 = (x_2)_0 + \int_1^P \frac{v_s - \bar{v}_2}{\partial\mu_2/\partial x_2} \qquad (14)$$

The values of v_s, the specific volume of the solid salt under pressure, were taken from the measurements by Adams and Gibson;[14] $\bar{v}_2$ is given in Table VI; $(x_2)_0$, the solubility at atmospheric pressure, was taken as 0.1076 according to the "International Critical Tables"; and $\partial\mu_2/\partial x_2$ was calculated from the data used above for the calculation of μ_1. From the e. m. f. data $\partial\mu_2/\partial x_2$ at $x_2 = 0.1076$ was found to be 273 joules. The coefficient was also computed, by the method described in the earlier paper, from the heat of solution of the salt and change of solubility with temperature. With $\Delta\bar{h}_2 = 112$ joules and $(dx_2/dt)_{satn.} = 0.00148$, $\partial\mu_2/\partial x_2$ at $x_2 = 0.1076$ was found to be 254. Probably more weight should be given to the first value, and we shall take $\partial\mu_2/\partial x_2$ as 265 joules at atmospheric pressure and at $x_2 = 0.1076$. The e. m. f. data allow us to calculate the change of $\partial\mu_2/\partial x_2$ with concentration. Thus at $x_2 = 0.10$, $\partial\mu_2/\partial x_2$ is 290, and at $x_2 = 0.15$ (by extrapolation) is 185. At pressures other than atmospheric the magnitude of $\partial\mu_2/\partial x_2$ was computed by numerical integration of the equation

$$\frac{\partial\mu_2}{\partial x_2} = \left(\frac{\partial\mu_2}{\partial x_2}\right)_0 + \int_1^P \frac{\partial v_2}{\partial x_2}\,dP \qquad (15)$$

The variation under pressure of $\partial\mu_2/\partial x_2$ for potassium sulfate at concentrations near saturation is considerably greater than for sodium chloride. In the present instance, an increase of pressure from 1 to 10,000 bars changes $\partial\mu_2/\partial x_2$ at $x_2 = 0.10$ to 502, and at $x_2 = 0.15$ to 380.

In Table X are shown the results for the solubility of potassium sulfate in water at pressures up to 12,000 bars, together with the most important steps in the calculation. The results above 10,000 bars were obtained by extrapolation of the data from which the solubility was determined. Since $\bar{v}_2$ and $\partial\mu_2/\partial x_2$ pertain to the saturation–concentration at each pressure, and since this concentration changes by a considerable amount under pressure, it was necessary to carry out the computation by a series of approximations. First, $\bar{v}_2$ and $\partial\mu_2/\partial x_2$ at $x_2 = 0.1076$ were used in equation (14), and a first approximation thus obtained. Then, new values of $\bar{v}_2$ and $\partial\mu_2/\partial x_2$ were calculated at the approximated x_2's, and the integration repeated. The third approximation differed very little from the second, and is the one shown in Table X.

[14] Adams and Gibson, *J. Wash. Acad. Sci.*, **21**, 387 (1931).

TABLE X

SOLUBILITY OF POTASSIUM SULFATE IN WATER AT VARIOUS PRESSURES

Temperature, 25°

Pressure in bars	v_s	$\bar{v}_2$ at satn.	$\bar{v}_2 - (\bar{v}_2)_{satn.}$	$\partial\mu_2/\partial x_2$ at $x_2 = 0.10$ (joules)	$\partial\mu_2/\partial x_2$ at satn. (joules)	$10^2 \Delta x_2$	x_2
1	0.3761	0.2722	0.1039	290	265	0.0	0.1076
1000	.3749	.3206	.0543	330	240	3.03	.138
2000	.3737	.3466	.0271	364	245	4.67	.154
3000	.3725	.3616	.0109	391	262	5.34	.161
4000	.3713	.3714	−.0001	414	281	5.55	.163
5000	.3702	.3779	−.0077	433	299	5.42	.162
6000	.3691	.3815	−.0124	449	318	5.09	.159
7000	.3681	.3842	−.0161	464	339	4.66	.154
8000	.3670	.3861	−.0191	478	360	4.16	.149
9000	.3660	.3872	−.0212	490	380	3.62	.144
10000	.3651	.3877	−.0226	502	400	3.05	.138
11000	.3641					(2.47)	(.132)

The Equilibrium Diagram.—The course of the freezing pressure curve for ice_{VI} and of the solubility curve of potassium sulfate is illustrated in Fig. 2. Initially the solubility rises rapidly with increase of pressure, but the rate of increase falls off, and attains a maximum at 3800 bars, at

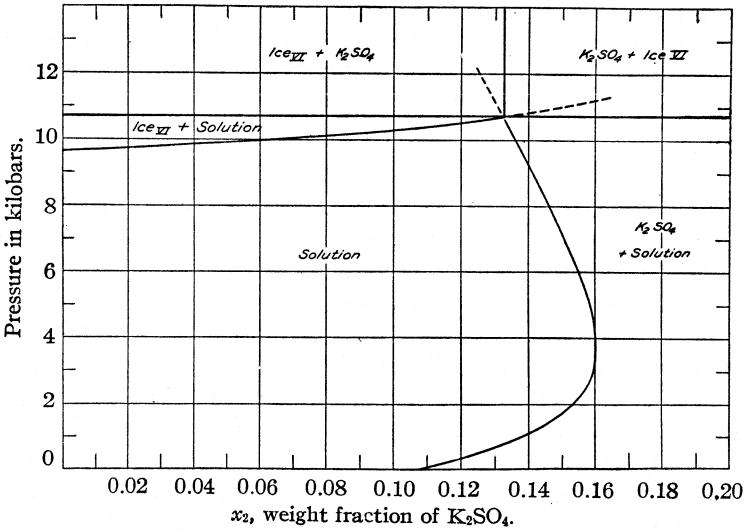


Fig. 2.—The equilibrium diagram for the system, K_2SO_4–H_2O, under pressure.

which point the solubility is 16.3%. At higher pressures the solubility diminishes steadily until the curve intersects the freezing pressure curve of ice_{VI} at P = 10,750 and x_2 = 13.3, and subsequent increase of pressure would cause complete solidification to a mixture of ice_{VI} and solid salt.

This invariant point is analogous to an ordinary eutectic in a temperature–concentration diagram, and may be called a pressure-eutectic. A comparison with the diagram for NaCl–H_2O shows the following differences: (1) in general appearance the diagram is much more simple, mainly on account of the lack of formation of a solid hydrate, such as was observed in the former system; (2) the variation of solubility is much greater in the present case, although a maximum solubility is attained at nearly the same pressure; (3) the total increase of freezing pressure of ice_{VI} is much less than with NaCl–H_2O (partly due to the low solubility of potassium sulfate), so that the eutectic pressure is not far above the freezing pressure of pure water.

Direct Determinations of Equilibrium

No direct measurements of the solubility of potassium sulfate under pressure were made, but a direct determination of the freezing pressure of a 10% solution was carried out by the method described in the previous paper.[15] The mean of two measurements, which differed by 19 bars, was 10,200 bars (rounded off to the nearest 10). The agreement with the indirect determination, 10,290 bars, is not quite as satisfactory as was expected. The discrepancy is probably mainly due to the uncertainty in the value of μ_1 at atmospheric pressure, especially in the concentrated solutions.

Since the eutectic pressure is so comparatively low it was found possible to make a direct determination of this also. All that was required was to continue to increase the pressure on the solution until sufficient ice_{VI} had frozen out to bring the concentration of salt in the solution up to the saturation value, whereupon the pressure remained constant although the volume was further decreased—provided equilibrium was attained. Figure 3 illustrates the procedure in determining the eutectic pressure and also the freezing pressure of the solution. The latter was at the point marked A in the diagram. As increasing amounts of ice_{VI} froze out the equilibrium pressure followed along the line AB, and at B was saturated with respect to the salt. The solid salt did not immediately precipitate, however; some supersaturation was observed as shown by the dotted prolongation of AB. After the solution had been allowed to remain undisturbed for about one hour, salt had crystallized out and the pressure had fallen to practically the equilibrium value. Along the line BC the pressure remained substantially constant and at C the solution had entirely solidified to a mixture of ice_{VI} and solid potassium sulfate. The directly measured eutectic pressure was 10,880 bars, which is to be compared with 10,750 bars, the result of the indirect determination. The agreement is not so close as in the determination of the freezing pressure of the 10% solution by the two methods. It may be noted that the eutectic pressure (by the indirect

[15] Adams, Ref. 1, pp. 3811 *et seq.*

determination) is dependent on the course of the solubility curve, which in turn is considerably affected by any uncertainty in the value of μ_2 at atmospheric pressure. The principal difficulty here arises from the necessity for extrapolating μ_2 into a region of concentration far beyond that in which it has been measured. Indeed, the weakest link in the chain of data used for the determination of equilibrium in systems under pressure is probably the simple physical properties of the concentrated solutions at atmospheric pressure.

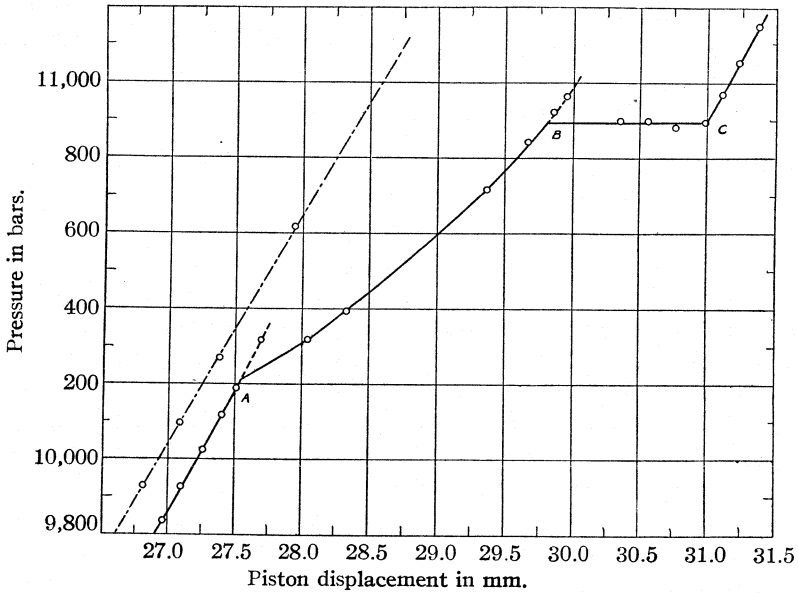


Fig. 3.—Diagram showing the method used in the direct determination of the freezing pressure of a 10% K_2SO_4 solution and also the eutectic pressure. The point A indicates the beginning of freezing, B the eutectic pressure and C complete solidification.

Summary

The compression of aqueous solutions of potassium sulfate was measured at pressures up to 10,000 bars, and from these measurements the fictive (partial) volumes and the chemical potentials of the two components were calculated according to the procedure described in a former communication.

Under pressure the fictive volume of the salt shows the same striking *increase* that was observed previously for sodium chloride. This phenomenon suggests that pressure causes solutions to become more nearly ideal.

From the values of the chemical potentials at various pressures the solubility curve of the salt and the freezing pressure curve of ice_{VI} were calculated, and an equilibrium diagram for the system, K_2SO_4–H_2O, under high-

pressure was constructed. Direct measurements of the eutectic pressure, and of the freezing pressure of a 10% solution, showed a fair agreement with the indirect determinations.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

THE USE OF THE ANTIMONY ELECTRODE IN THE ELECTROMETRIC ESTIMATION OF MAGNESIUM[1]

BY B. B. MALVEA AND JAMES R. WITHROW

RECEIVED JANUARY 13, 1932 PUBLISHED JUNE 6, 1932

Introduction.—Extended work on "lime" in this Department demanded determination of magnesium at frequent intervals, especially in control work. The standard methods for such determinations were long and tedious. Their precision also has been a subject of controversy in recent years. The ordinary hydrogen electrode method suggested itself but was complicated and too highly sensitive to permit of ready handling without error. The convenience and simplicity of the antimony electrode made it desirable to investigate its application to the determination of magnesium. The present paper deals with this investigation.

Literature.—Hildebrand and Harned[1a] were the first to use the hydrogen electrode method for the determination of magnesium in the presence of calcium in dolomite and limestone. They considered their method as fairly rapid and accurate. H. S. Harned[2] applied the conductimetric method for the determination of magnesium in magnesium sulfate. According to him, the value "agreed with that from a gravimetric analysis." Later I. M. Kolthoff[3] confirmed the above work and stated that satisfactory results were obtained by precipitating the magnesium hydroxide with excess standard alkali, filtering and titrating back with standard acid. Gilbert A. Freak,[4] using the conductimetric method, studied the "effect of dilution in electro-titrimetric analysis." I. M. Kolthoff[5] confirmed Pinkhoff's result (Diss., Amsterdam, 1919) and made an extensive study of this magnesium reaction, using the hydrogen electrode. He declared that the method was of little practical use.

The Use of the Antimony Electrode.—The antimony electrode has found application in recent years in electrometric work. For the most

[1] Original manuscript received February 18, 1931.

[1a] Hildebrand and Harned, *Proc. 8th Intern. Congr. App. Chem.*, **1**, 217 (1912).

[2] Harned, THIS JOURNAL, **39**, 252–266 (1917).

[3] Kolthoff, *Z. anorg. allgem. Chem.*, **112**, 172 (1920).

[4] Freak, *J. Chem. Soc.*, **115**, 55–61 (1919).

[5] Kolthoff, *Rec. trav. chim.*, **41** (1922), and Kolthoff and Furman in "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1926.

part, the workers starting with Uhl and Kestranek[6] have used it for the measurement and standardization of P_H values or latterly for the measurement of high alkalinity in the black liquors from paper pulp cooks, where the hydrogen electrode for one reason or another failed. Among the chief workers with the antimony electrode may be mentioned E. J. Roberts and F. Fenwick,[7] who showed the special advantages of the antimony electrode. Kolthoff and Hartong[8] have made extensive studies of the application of the antimony electrode. K. W. Franke and J. J. Willaman[9] studied the effect of the nature of the metal constituting the electrode and also the effect of various gases in titration work. Lucius W. Elder, Jr.,[10] says "The antimony electrode shows an abnormal titration curve in acid solutions of ferric chloride, probably because of the presence of pentavalent antimony in the solutions."

However, we are not aware of any published work on the use of the antimony electrode for such estimations as that of magnesium.

Experimental

Apparatus.—The usual set-up for potentiometric titrations, using a calomel half-cell, was employed. The antimony electrode was made from commercial "stick" antimony sand-papered to a smooth surface.

Procedure.—A quantity each of standard solutions of chemically pure magnesium chloride (hexahydrated crystals) and calcium chloride was prepared such that one cc. of each contained a definite amount of MgO and CaO. The determination of MgO in the stock solution was made according to the standard gravimetric method and that of CaO by titration of the precipitated oxalate with a standard solution of potassium permanganate. From these stock solutions several mixtures of known strength of MgO and CaO were prepared. The amount of magnesium was kept constant but that of calcium was allowed to vary. The magnesium in these mixtures was then estimated. As a check several gravimetric–volumetric analyses and estimations with the hydrogen electrode were made side by side and the results compared.

To make a determination, measured amounts of magnesium and calcium solutions were diluted to 150 cc., acidified with a few drops of dilute hydrochloric acid and methyl orange indicator added. When the e. m. f. had become constant, a normal (or 0.1 *N* with dilute solutions) solution of sodium hydroxide free from carbonate was added in portions of 0.2 cc., allowing sufficient time for the e. m. f. readings to become constant, which required from two to ten minutes. The potential was plotted against volume of alkali used.

Determination of Alkali Used for Magnesium Precipitation.—The curve obtained showed two inflections corresponding to the beginning and to the end of the precipitation of magnesium hydroxide. A vertical line projected through the point of first inflection to the horizontal axis (alkali) gave the initial alkali reading to be used in calculation. The other inflection ordinarily was not quite so sharp as the first and consequently it was a little difficult to locate the exact end-point of the titration. In our method an "oscula-

[6] Uhl and Kestranek, *Monatsh*, **44**, 29 (1923).

[7] Roberts and Fenwick, THIS JOURNAL, **50**, 2126 (1928).

[8] Kolthoff and Hartong, *Rec. trav. chim.*, **44**, 113 (1925).

[9] Franke and Willaman, *J. Ind. Eng. Chem.*, **20**, 87 (1928).

[10] Elder, *Trans. Am. Electrochem. Soc.*, **57**, 383 (1930).

tory" tangent between the two arms of the inflection was drawn and from a point midway between the points of contact of this tangent and the curve a vertical line was projected to the horizontal axis. The point where this line met the horizontal axis gave the final reading of the alkali. As a check, however, by plotting $\Delta E/\Delta V$ against volume a differential curve was obtained which showed two well-defined peaks. Vertical lines projected through these points to the horizontal axis (volume) gave the volume of alkali used for titration. From this the amount of magnesium present in the solution could be easily calculated.

Reagents.—All reagents and chemicals used were chemically pure. The strength of potassium permanganate used for volumetric estimation of calcium was 0.099 normal. Standard solutions of magnesium and calcium chloride contained 0.01 g. of MgO and CaO per cc., respectively (in dilute solutions 0.001 g.). Standard sodium hydroxide was 1.01 normal (0.118 normal in the case of dilute solutions).

Data

From a series of curves obtained as a result of fourteen different runs, an example is included here. The results have been summarized in the table.

The accompanying figures illustrate the curves obtained. The differential curve, Fig. 2, shows how the amount of alkali used for magnesium precipitation was ascertained. This value is the same as that obtained by the "osculatory" tangent method, Fig. 1.

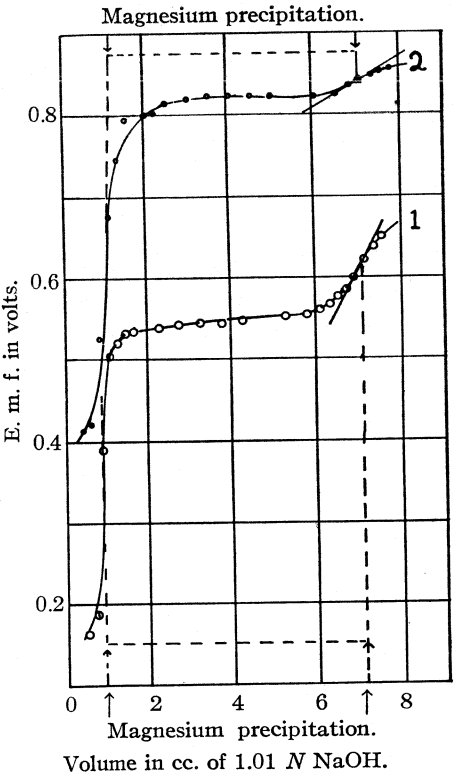


Fig. 1.—Electrometric estimation of magnesium.

	NaOH used, cc.	MgO estimated, g.	Error, %
Curve 1, hydrogen electrode	6.2	0.125	0
Curve 2, antimony electrode	6.0	0.121	−3.2

Runs 1–9 were made using fairly strong solutions. Runs 10–14 were with dilute solutions. The results indicate that the antimony electrode gave fairly accurate values for magnesium when it was alone in strong or in dilute solutions. However, if the dilution was lower than 0.01 g. of MgO in 150 cc. of solution, the results were not dependable. When calcium was present, in fairly strong solutions, estimations could be made until the concentration of calcium was as much as eight times that of magnesium. The maximum error was under 3.5%. When the concentration of calcium was increased to twenty-five and fifty times that of magnesium,

TABLE I

COMPARATIVE RESULTS OF MAGNESIUM ESTIMATION

No.	Content of mixture MgO, g.	CaO, g.	NaOH used Sb elect., cc.	H_2 elect., cc.	MgO estimated Sb elect., g.	H_2 elect., g.	Grav., g.	Error, % Sb elect.	Error, % H_2 elect.
1	0.125	0.000	6.2	6.0	0.125	0.121	0.125	0	−3.2
2	.125	.125	6.0	6.25	.121	.126	.125	−3.2	0.8
3	.125	.250	6.0	5.9	.121	.120	.126	−3.2	−4.0
4	.125	.500	6.2		.125			0	
5	.125	1.000	6.0		.121			−3.2	
6	.010	0.250	Not definite		Could not be estimated				
7	.010	.500	Not definite		Could not be estimated				
8	.010	.000	0.6		.118			−6.0	
9	.010	.000	4.3[a]		.010			0	
10	.010	.000	4.25		.010			0	
11	.005	.000	1.95		.005			0	
12	.010	.010	4.55		.011			10	
13	.010	.050	4.8		.011			10	
14	.010	.100	Not definite		Could not be estimated				

[a] Dilute sodium hydroxide in this and subsequent estimations.

the method failed. In dilute solutions of magnesium, if calcium was present even to the extent of equivalent proportions with magnesium, the results showed high errors and were not dependable.

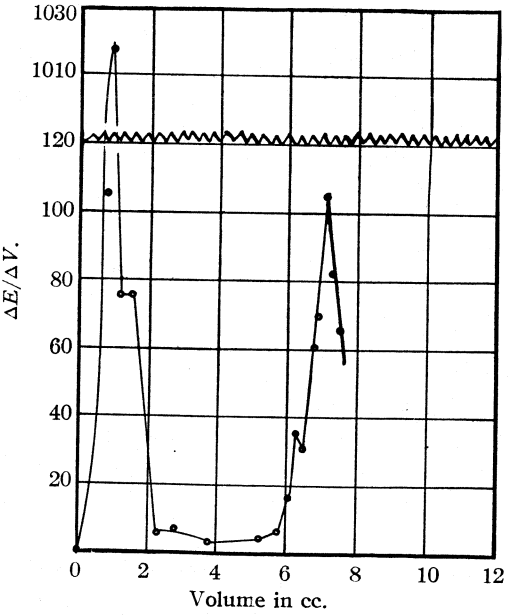


Fig. 2.—Differential curve for Curve 1; volume of alkali, ±6.2 cc.

Several advantages over the hydrogen electrode characterized the antimony electrode—simplicity of construction, ease of manipulation, free-

dom from the necessity of electrodeposition of a metal, apparent absence of poisoning effect, freedom from both manipulation and control of a gas phase.

Summary

1. The antimony electrode made of commercial stick antimony was a satisfactory substitute for the hydrogen electrode in the electrometric estimation of magnesium in its salts and in mixtures of calcium and magnesium salts.

2. Calcium could be present to the extent of eight to twenty-five times the amount of magnesium.

3. The minimum concentration of MgO was 0.10 g. in 150 cc. of solution. At low dilutions the results were unsatisfactory if calcium was present in any appreciable amount, or was even equivalent in amount to the magnesium.

COLUMBUS, OHIO

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 306]

THE FREE ENERGY, HEAT CONTENT AND ENTROPY OF IODINE MONOCHLORIDE

BY JOHN MCMORRIS AND DON M. YOST

RECEIVED JANUARY 19, 1932 PUBLISHED JUNE 6, 1932

Introduction

The absorption bands of iodine monochloride have been studied by Gibson and Ramsperger,[1] Wilson,[2] Curtis and Darbeyshire[3] and Curtis and Patkowski;[4] and from the results of this work the thermodynamic constants of iodine monochloride may be computed. The uncertainties in interpretation of these spectroscopic data, however, make it desirable that the thermodynamic constants be also derived from some entirely independent source. Two separate chemical studies of this problem are presented in this paper.

The combination in the vapor phase of iodine and chlorine to form iodine monochloride is not accompanied by a change in the total number of molecules. Since there is no total pressure change, the methods employed in this research for studying the reaction are necessarily indirect.

The first method used depends upon the presence of solid barium chloroplatinate which is in equilibrium with the chlorine, barium chloride and platinum, of which only the chlorine reacts with iodine. The dissocia-

[1] Gibson and Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

[2] Wilson, *ibid.*, **32**, 611 (1928).

[3] Curtis and Darbeyshire, *Trans. Faraday Soc.*, **27**, 77 (1931).

[4] Curtis and Patkowski, *ibid.*, **25**, 725 (1929); *Nature*, **127**, 707 (1931).

tion pressures of barium chloroplatinate as a function of temperature have already been determined by Gire.[5] Starting with pure iodine and barium chloroplatinate, two molecules of iodine monochloride will result for each molecule of iodine reacting and the equilibrium state can then be determined by measuring the resulting pressure increase. This will be designated in the later discussion as Method I.

A study was also made of the reversible gas phase reaction

$$2NOCl + I_2 = 2NO + 2ICl$$

and the results were combined with the data of Dixon[6] for the reaction

$$2NO + Cl_2 = 2NOCl$$

thus making it possible to calculate the equilibrium constants at various temperatures for the reaction

$$\frac{1}{2}I_2 + \frac{1}{2}Cl_2 = ICl$$

This will be designated as Method II. In all cases iodine monochloride was observed in the reaction vessels at the conclusion of the experiments.

An attempt was also made to study the reaction between phosgene ($COCl_2$) and iodine, but it was found to be immeasurably slow at temperatures below 200°.

Experimental Method I

A Pyrex bulb of known volume was charged with about seven grams of very dry barium chloroplatinate. One side arm of small bore Pyrex tubing connected the reaction bulb to a glass diaphragm click gage which was in turn connected to the manometer system. Another side arm contained an evacuated glass capsule within which was an accurately weighed amount of pure iodine. The capsule had a tip which could be broken readily by means of a glass-inclosed iron plunger and an external solenoid. A tube by-passing the click gage was provided so that, in evacuating the reaction vessel, no excess pressure would be exerted on either side of the diaphragm. An electric furnace, built according to the recommendations of Gray,[7] surrounded the reaction bulb. Since the temperature required for the reaction to be conveniently measurable was in the region of 400°, the inclusion of the click gage within the furnace was impracticable. The gage was therefore allowed to project a few centimeters from the furnace and was separately heated to a constant temperature of 150° by a small second furnace immediately adjoining the larger one.

The click gage was accurately calibrated before connecting the gage to the reaction bulb. The constants for the gage used were found to be independent of the temperature over the range from 25 to 175°. After sealing on the click gage, the system was evacuated and the large furnace brought to a temperature of 300°. The system was re-evacuated every few hours for a period of three days, after which time the gain in pressure in the system overnight was less than 0.1 mm. The furnace was then heated to 490°, producing a pressure of chlorine from barium chloroplatinate of about 20 mm., the click gage was heated to 150° and the chlorine was pumped off several times. The by-pass tube was then sealed off, the furnace cooled, and the constants of the click gage re-

[5] Gire, *Ann. chim.*, **4**, 186 (1925).

[6] Dixon, *Z. physik. Chem.*, Bodenstein Festband, 679 (1931).

[7] Gray, Publication of Bureau of Standards, S219.

determined. All experiments were carried out at a temperature below 490°; the prolonged baking out doubtless prevented any interference from the presence of water vapor or other foreign gas at the lower temperatures. During these preliminary manipulations, the temperature variation over the length of the large furnace was also determined and the ends were found to be less than one degree cooler than the center. The temperatures were measured by means of chromel–alumel thermocouples calibrated against standardized thermometers, the boiling point of purified naphthalene and the freezing point of zinc.

When the furnace had cooled to room temperature, the iodine capsule was broken by means of the magnetic device. The iodine was driven over into the reaction bulb and the side arm was then sealed off and removed. The furnace surrounding the click gage was heated to 150° and the reaction bulb was heated to the temperature of the experiment.

The chemicals used were of high quality. The iodine was of analytical quality marked 99.97% pure. The barium chloroplatinate was prepared by carefully neutralizing chloroplatinic acid with barium hydroxide solution and dehydrating the resulting solution in a vacuum desiccator over sulfuric acid.

Results of the Experiments

The reaction whose equilibrium constant is to be found is

$$ICl(g) = {}^1/_2\, I_2(g) + {}^1/_2 Cl_2(g) \qquad (1)$$

The corresponding mass action expression is

$$\frac{(I_2)^{1/2}(Cl_2)^{1/2}}{(ICl)} = K \qquad (2)$$

The partial pressure of the chlorine at any given temperature is fixed and is calculated from the following formula, which was constructed from Gire's data

$$\log_{10} p_{mm} = -\frac{6171}{T} + 9.356 \qquad (3)$$

Some pressure measurements, made at various temperatures before admitting iodine, confirmed Gire's results.

If p_1 is the partial pressure of chlorine, p_2 the calculated pressure of iodine for no reaction and p_3 the total pressure in the system, then

$$2(p_3 - p_1 - p_2) = \text{partial pressure of ICl} \qquad (4)$$
$$2p_2 - p_3 + p_1 = \text{partial pressure of } I_2 \qquad (5)$$

In Table I are presented the results of the experiments. Equilibrium was approached from both directions but the extreme slowness of the reaction made the exact attainment of equilibrium somewhat uncertain. Five or six days were usually required to reach a constant pressure in the system. The most accurate values of K are probably those for 681.7 Å. and 682.8 Å., not merely because of their good agreement but also because the rate of reaction is much greater than at the lower temperatures and because the magnitudes of the various partial pressures are less subject to errors than those at the higher temperatures. It is to be noted that the pressure of chlorine varied twenty-fold over the range

of temperatures investigated. Quantities of iodine differing by 20% were used in two different sets of experiments. All pressures are expressed in mm. of mercury.

TABLE I

Temperature, °K.	681.7	641.1	667.9	667.6	736.6	746.4	682.8
Pressure of $Cl_2 = p_1$	2.01	0.54	1.31	1.30	9.51	12.22	2.08
Pressure (initial) of $I_2 = p_2$	205.1	192.8	200.9	158.5	174.7	177.3	162.1
Total pressure (observed) $= p_3$	350.8	280.9	352.6	239.5	342.3	356.6	281.6
Pressure of ICl	287.4	175.0	300.8	159.4	316.2	334.2	234.8
Pressure of I_2 (final)	61.4	105.3	50.5	78.8	16.6	10.2	44.7
K	0.0386	0.0431	0.0270	0.0633	0.0398	0.0335	0.0411
$\log_{10} K$	−1.41	−1.37	−1.57	−1.20	−1.40	−1.42	−1.39

Experimental Method II

The reaction vessel of known volume consisted of a Pyrex bulb equipped with a click gage, a closed side arm, an open side arm and a tube by-passing the click gage. The closed side arm contained a capsule inclosing very pure nitrosyl chloride and a glass incased iron plunger. After introducing through the open side arm an evacuated glass capsule containing a known weight of iodine, the side arm was sealed off. The apparatus was then evacuated and baked out. The by-pass tube was sealed off and removed. The nitrosyl chloride in the side arm was then frozen with liquid air, the capsule broken, and the nitrosyl chloride allowed to evaporate. After coming to room temperature the pressure and temperature of the nitrosyl chloride were carefully determined. The iodine capsule was broken by shaking the reaction bulb. The apparatus was then connected to the manometer system and both the reaction bulb and gage were submerged in an electrically heated oil thermostat.

Experiments were made at various temperatures and with two separate loadings of the apparatus. The reaction was found to be rapid and readily reversible, less than an hour being required for constant pressure to be attained. Most of the final readings were made, however, after twenty-four hours with the given temperature held constant to ±0.2°.

The iodine used was of the same quality as that previously employed. The nitrosyl chloride was kindly furnished by Mr. J. Leermakers from the material prepared by him for the determination of its absorption spectrum.[8]

Results of the Experiments

From these experiments the equilibrium constant can be calculated for the reaction

$$2NO + 2ICl = 2NOCl + I_2 \qquad (6)$$

and is given by the expression

$$\frac{(NOCl)^2(I_2)}{(NO)^2(ICl)^2} = K_1 \qquad (7)$$

Starting with NOCl and I_2, the total pressure measured will be greater by Δp than the sum of the NOCl and I_2 pressures calculated for no reaction. If p_1 and p_2 are the pressures of iodine and nitrosyl chloride, respectively, assuming no reaction, then 2 Δp is equal to the partial pressure of the iodine monochloride and also that of the nitric oxide while

[8] Leermakers and Ramsperger, THIS JOURNAL, **54**, 1837 (1932).

$p_1 - \Delta p$ and $p_2 - 2\Delta p$ give the partial pressures of the iodine and nitrosyl chloride, respectively. All pressures are expressed in millimeters and the values of K_1 in atmospheres.

TABLE II

RESULTS OF THE EQUILIBRIUM MEASUREMENTS

	Initial pressure			Pressure increase,	Equilibrium pressure of				
T, °C.	I_2	NOCl	Pressure obs.	Δp	NO	ICl	I_2	NOCl	K_1, atm.	$\log_{10} K_1$
136.4	162.2	320.8	588.8	105.8	211.6	56.4	109.2	0.255	−0.593
136.9	156.9	321.2	582.5	104.4	208.8	52.5	112.4	.265	− .577
145.5	160.2	328.0	598.1	109.9	219.8	50.3	108.2	.192	− .717
149.0	167.2	330.7	611.8	113.9	227.8	53.3	102.9	.159	− .799
153.6	169.0	334.3	620.4	117.1	234.2	51.9	100.1	.131	− .883
164.4	167.4	342.8	632.8	122.6	245.2	44.8	97.6	.0897	−1.047
178.8	172.9	354.0	658.3	131.4	262.8	41.5	91.2	.0550	−1.260

The equation relating the equilibrium constant K_1 in atmosphere units with temperature is

$$\log_{10} K_1 = \frac{2888}{T} - 7.638 \qquad (8)$$

Thermodynamic Constants of Iodine Monochloride

J. K. Dixon[6] recently has made a very careful study of the reversible reaction

$$2NOCl = 2NO + Cl_2$$

and finds that the equilibrium constants $K_2 = (NO)^2(Cl_2)/(NOCl)^2$ in atmospheres may be represented as a function of the temperature by the equation

$$\log_{10} K_2 = -\frac{3860}{T} + 3.348 \log_{10} T - 0.002457T - 1.1275 \qquad (9)$$

It follows at once that $(K_1K_2)^{1/2} = K$ where K is the equilibrium constant for reaction (1).

In Table III are given the data leading to values of K at the various temperatures investigated by Method II.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF NITROSYL CHLORIDE AND IODINE MONOCHLORIDE

Temp., °C.	$10K_1$	$\log_{10} K_1$	$10^4 K_2$	$\log_{10} K_2$	$10^3 K$	$\log_{10} K$
136.4	2.55	−0.593	3.09	−3.510	8.89	−2.051
136.9	2.65	− .576	3.16	−3.500	9.16	−2.038
145.5	1.91	− .718	5.04	−3.298	9.82	−2.008
149.0	1.60	− .796	6.08	−3.216	9.86	−2.006
153.6	1.31	− .882	7.66	−3.116	10.02	−1.999
164.4	0.898	−1.047	13.12	−2.882	10.84	−1.965
178.8	.552	−1.258	25.71	−2.590	11.91	−1.924

When the values of $\log_{10} K$ in the last column are plotted against the corresponding reciprocal temperatures, a straight line may be drawn through the points with an uncertainty of about 10% in the slope. The

points for the three highest temperatures fall very closely on a straight line from whose slope ΔH is found to be 2620 cal. However, the remaining four points fall somewhat to one side of this line so that the best linear representation of all the points is a line whose slope gives ΔH the value 2500 cal. Considering the fact that the whole temperature range is only 42°, not a great deal of reliance should be placed on any value of ΔH computed from the results of these experiments alone.

A value of ΔH obtained by combining the data from experiments using Method I with those using Method II is probably much more reliable, since the extreme temperature interval is then 337° and the constants for each set of experiments are probably reasonably good. The value of ΔH so derived is 3125 cal. The experimental error involved in this result is estimated to be between ±5 and ±10%, the value of ΔH given being probably low.

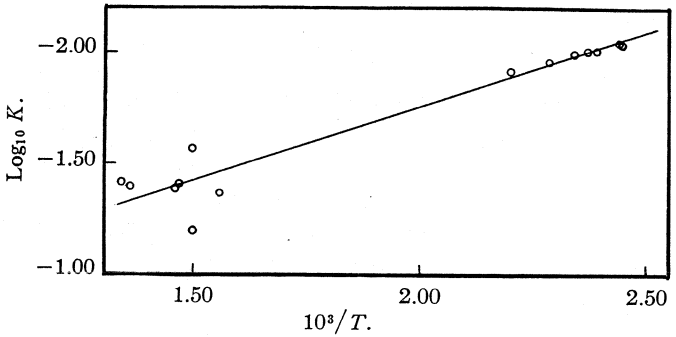


Fig. 1.—Equilibrium constants for the dissociation of gaseous iodine monochloride.

A graph of $\log_{10} K$ against $1/T$ for all experiments by both methods is shown in Fig. 1.

The free energy equation which best represents the experimental data for the reaction

$$\tfrac{1}{2}\,I_2(g) + \tfrac{1}{2}Cl_2(g) = ICl(g) \qquad (10)$$

is

$$\Delta F^\circ = -3125 - 1.77T \qquad (11)$$

Since for a reaction of this type ΔC_p is certainly small, the absence of non-linear terms does not affect the validity of the equation even over a fairly large temperature range.

The spectroscopical investigations of iodine monochloride make it possible to derive, quite independently, a free energy equation for reaction (11). Gibson and Ramsperger[1] and Wilson[2] have determined the absorption limit corresponding to the dissociation of the monochloride. If we take their value and assume that the dissociation results in normal atoms and if, in accordance with the extensive work of Patkowski

and Curtis,[4] the absorption is due to molecules in their lowest vibrational state, then the following thermochemical equations may be written.

$$\begin{aligned} \text{I (g)} + \text{Cl(g)} &= \text{ICl}(g, n'' = 0) & \Delta H &= -49590 \text{ cal.} \\ {}^1/_2\,\text{I}_2\text{(g)} &= \text{I(g)} & \Delta H &= 17496 \text{ cal.}^{9} \\ {}^1/_2\,\text{Cl}_2\text{(g)} &= \text{Cl(g)} & \Delta H &= 28435 \text{ cal.}^{10} \\ \text{Hence } {}^1/_2\,\text{I}_2\text{(g)} + {}^1/_2\,\text{Cl}_2\text{(g)} &= \text{ICl}(g, n'' = 0) & \Delta H &= -3461 \text{ cal.} \end{aligned}$$

This value of -3461 cal. refers to the absolute zero of temperature and must be corrected to ordinary temperatures before a comparison with the thermochemical value may be made. It may be shown, however, that the heat of the reaction depends but little on the temperature and the correction is therefore very small. The agreement between the spectroscopic and thermochemical values of ΔH is quite satisfactory.

If the dissociation of the iodine monochloride by radiation were to result in an activated chlorine atom, the value of ΔH would be -2041 cal. or -951 cal. depending on whether the absorbing molecule were in the first or in the lowest vibrational state. If, on the other hand, the dissociation products are normal atoms, then ΔH has the value -4551 cal. if the absorbing molecule is in the first vibrational state and -3461 cal. if in the lowest state. All of these values except the last differ from that obtained from the equilibrium measurements by an amount considerably greater than corresponds to the experimental error. The present results show, therefore, that the absorption limit results from a molecule in its lowest vibrational state being dissociated into normal atoms of iodine and chlorine.[11] It may also be added that Thomsen's calorimetric result combined with accurately known heat data gives $\Delta H = -3748$ cal., which gives added support to this conclusion.

It is also possible to compare the present value of 1.77 cal./deg. for ΔS of reaction 10 with that derived spectroscopically. Using Giauque's[12] values of 62.29 cal./deg. and 53.31 cal./deg. for the entropies of iodine and chlorine vapors, respectively, and the value 59.2 cal./deg. for iodine monochloride vapor which we have calculated from spectroscopic data,[11] a value of $\Delta S = 1.40$ cal./deg. is found. This is in satisfactory agreement with the thermochemical value.

The two standard free energy equations obtained from entirely independent types of experiments are then

$$^1/_2\,\text{I}_2\text{(g)} + {}^1/_2\,\text{Cl}_2\text{(g)} = \text{ICl(g)} \qquad (10)$$

$$\Delta F^\circ = -3125 - 1.77T \text{ (thermochemical measurements)} \qquad (12)$$

$$\Delta F^\circ = -3461 - 1.40T \text{ (spectroscopic measurements)} \qquad (13)$$

---

[9] Brown, *Phys. Rev.*, **38**, 709 (1931).

[10] Sponer, Landolt–Börnstein–Roth, "Phys. Chem. Tab.," Julius Springer, Berlin, 1931, Part 2, second Ergänzungsband, p. 1615.

[11] This same behavior is also observed in the case of iodine monobromide. *Cf.* Badger and Yost, *Phys. Rev.*, **37**, 1548 (1931).

[12] Giauque, THIS JOURNAL, **53**, 507 (1931); **54**, 1731 (1932).

The thermodynamic constants of iodine monochloride may be calculated from the present results by combining them with the following thermal data. For iodine the values given in a previous paper[13] will be used and for the entropy of chlorine we use the value 53.31 cal./deg. employed above. The vapor pressure of liquid iodine monochloride has been accurately measured by one of us (D. M. Y.)[14] and is given by the empirical equation

$$\log_{10} p_{mm} = -\frac{2079.7}{T} + 8.5038 \qquad (14)$$

from which the free energy change attending vaporization at 25° has been calculated. Thomsen's[15] value for the heat of formation of the monochloride is also presented but not used in any of the calculations. We use 2668 cal.[16] for the heat of fusion of the solid monochloride at the melting point, 27.2°.

Table IV contains the so-calculated thermodynamic constants at 25° (expressed in calories) for one mole of the substance given in the first column. The reference states are indicated in each case. In the case of entropy values the state referred to is that indicated in the first row, the gases being present at a pressure of one atmosphere. The values for the heat contents given in parentheses are based on Thomsen's determination of the heat of formation of the liquid monochloride and are not employed elsewhere in the table.

TABLE IV

THERMODYNAMIC CONSTANTS OF IODINE MONOCHLORIDE AT 25°

Substance	ICl(g)	ICl(g)	ICl(l)	ICl(s)
Reference substances	I_2(g) Cl_2(g)	I_2(s) Cl_2(g)	I_2(s) Cl_2(g)	I_2(s) Cl_2(g)
Free energy (thermochemical)	−3653	977	− 867	− 887
Free energy (spectroscopical)	−3879	751	−1093	−1113
Heat content (thermochemical)	−3125	4313	−5207	−7875
	(−3748)	(3690)	(−5830)	(−8498)
Heat content (spectroscopical)	−3461	3977	−5543	−8211
Entropy (thermochemical)	59.6	59.6	57.0	48.1
Entropy (spectroscopical)	59.2	59.2	56.6	47.7
Heat of vaporization			9520	12,188

Discussion

As pointed out in a former paper,[13] the entropies of the diatomic interhalogen compounds in the gaseous state appear to lie between those of the diatomic elements from which they are formed, and the data for iodine

[13] McMorris and Yost, THIS JOURNAL, **53**, 2625 (1931).

[14] The experiments were carried out with the assistance of Mr. John B. Hatcher and the results have not been published. The values calculated from the equation agree with the observations to within the limits of experimental error ±0.2 mm. The equation is valid over the temperature range 0 to 70°, the liquid being supercooled below 27.2°, the melting point.

[15] Thomsen, *Ber.*, **15**, 3021 (1882).

[16] "International Critical Tables," 1929, Vol. V, p. 131.

monobromide and bromine monochloride were adduced in support of this statement. The value obtained for iodine monochloride is also in complete accord with this ordering of the entropies. The values of the entropy changes attending the formation of iodine monobromide and monochloride from the gaseous diatomic elements do not differ greatly (1.74, 1.77 (1.40)) and this fact might indicate that the same would be true for bromine monochloride and chlorine monofluoride, but the value calculated for bromine monochloride is less numerically than those just given and of opposite sign. However, the data available[17] are stated to be in error by an amount that could give a positive value for ΔS of the order of magnitude found for iodine monobromide and chloride.

In Table V are given the entropy values for the halogens and diatomic interhalogen compounds at 25° and one atmosphere.

TABLE V

ENTROPIES OF THE HALOGENS AND DIATOMIC INTERHALOGEN COMPOUNDS AT 25° AND ONE ATMOSPHERE

Substance	I_2	IBr	ICl	Br_2	BrCl	Cl_2	ClF	F_2
Entropy	62.29	62.2	59.15	58.63	56.9	53.31	?	48.0

It is to be noted that the order of the substances is that which would obtain if the chemical and physical properties were used instead of the entropies.

Summary

The equilibrium between barium platinic chloride, barium chloride, platinum, gaseous iodine and iodine monochloride, and that between nitrosyl chloride, nitric oxide, iodine and iodine monochloride have been measured. From the results the free energy equation for the reaction $^1/_2\,I_2(g) + {}^1/_2\,Cl_2(g) = ICl(g)$ has been found to be $\Delta F^\circ = -3125 - 1.77T$.

This resulting value of ΔH (−3125 cal.) was used to interpret existing spectroscopical data. A free energy equation, $\Delta F^\circ = -3461 - 1.40T$, was then derived using spectral data alone.[18] The agreement between the two equations is satisfactory.

[17] Jost, *Z. physik. Chem.*, [A] **153**, 143 (1931).

[18] W. G. Brown, in a recently received private communication, has kindly given us the results of his recent spectroscopic investigation of iodine monochloride, bromine and chlorine. He finds the entropies of these substances to be 59.15, 58.63 and 53.29 cal./deg., respectively. Using his newly determined values for the entropies and heats of dissociation of iodine monochloride and chlorine, the standard free energy equation for reaction (10) becomes $\Delta F^\circ = -3280 - 1.36T$. The value $\Delta H = -3280$ cal. is in excellent agreement with the one derived from the results of the equilibrium experiments, −3125 cal. The new data have been used in reconstructing Table V but are not employed elsewhere. The new entropy value for bromine has changed those for iodine monobromide and bromine monochloride, but this does not, of course, affect the free energy equations for the latter substances.

With iodine and chlorine in their standard states of solid and gas, the free energies of formation of the various forms of iodine monochloride as determined by physical chemical methods are as follows: ICl(g), 977 cal.; ICl(l), −867 cal.; ICl(s), −887 cal.

The degree of dissociation of iodine monochloride gas into gaseous iodine and chlorine has the value 0.42% at 25° and 1.58% at 100°.

The entropy of ICl(g) at 25° and one atmosphere is 59.6 cal./deg. (59.2 cal./deg. spectroscopical).

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CRYSTAL STRUCTURE OF RHOMBIC AMMONIUM NITRATE

BY C. D. WEST

RECEIVED JANUARY 28, 1932 PUBLISHED JUNE 6, 1932

No x-ray measurements on the rhombic form (IV) of ammonium nitrate have been published other than the three axial lengths. In addition to rounding out the univalent nitrate group, a complete structure is desirable for the interpretation of some of the unusual properties of this compound, such as birefringence, polymorphism and plastic deformation.

Crystallographic.—According to Groth the crystals are of the rhombic bipyramidal class, axial ratios 0.9092 : 1 : 1.0553, density 1.725, optic axial plane (100), acute bisectrix b. Bowen[1] found $2V = 35°$ and the refractive indices: electric vector parallel to b, $\alpha = 1.41$; parallel to a, $\beta = 1.61$; parallel to c, $\gamma = 1.64$. This form is stable only in the interval −16 to +32°.

Methods.—Recrystallization from water at room temperature gave suitable (110) prisms. Molybdenum radiation was employed exclusively; it was filtered in taking powder photographs and a set of 30° oscillation diagrams about the three axes. In a set of Laue patterns with the primary beam nearly parallel to the three axes, the minimum wave length was 0.30 Å. Intensitites of reflections were estimated visually. All Miller indices refer to the above axes.

Lattice Constants.—The constants determined from zero lines of accurate rotation photographs are: $a = 4.92_8$, $b = 5.43_4$, $c = 5.73_2$, ratios 0.9069 : 1 : 1.0548, $Z = 2$, $V = 76.7$, density = 1.720. The former are identical with Bragg's values to three figures.[2]

Choice of Structure.—The only systematic extinctions noted were for $(0kl)$ when $k + l$ is odd; assuming holohedral symmetry this indicates V_h^{13}. In disposing the atoms in this space-group primary consideration was

[1] N. L. Bowen, *J. Phys. Chem.*, **30**, 722 (1926).

[2] W. H. Bragg, *Trans. Faraday Soc.*, **20**, 59 (1924).

given to intensity data. It is probable that the nitrate group is a triangle of side 2.10 Å. with the distance between oxygen atoms in different groups greater than 3.2 Å.[3] It has been shown that some nitrates owe their strong double refraction to the arrangement of the nitrate groups in parallel planes, the ray with the electric vector parallel to these planes being the slower, that with the vector perpendicular to them the faster; also the molecular birefringence, $R\omega - R\epsilon$, tends to be constant as the metal ion is changed.[4] Bragg's extended table proves that ammonium nitrate follows this rule; it is thus to be expected that in it the nitrate planes lie perpendicular to *b*.

	M/ρ	ω	ε	Rω	Rε	Rω−Rε
$LiNO_3$	28.9	1.735	1.435	11.60	7.54	4.06
$NaNO_3$	37.45	1.587	1.336	12.58	7.75	4.83
KNO_3	47.85	1.506	1.335	14.36	9.90	4.46
NH_4NO_3	46.35	1.625	1.41	16.38	11.48	4.90

There are two orientations of the crystal axes *abc* in the structure axes XYZ that give the extinctions noted, (A) *abc* in ZYX and (B) *abc* in YZX. There are two arrangements which give nitrate groups of the desired configuration; taking point designations from Wyckoff and indicating ammonium and nitrate nitrogens by Nh and No, respectively, these are (I) Nh in (*a*), No and O in (*b*), O in (*e*) and (II) Nh in (*b*), No and O in (*a*), O in (*f*). Of the four arrangements IA and IIB have the same structure factor, which is constant for sets of reflections where only *l* varies by 2; they are excluded by the following sets: 101 absent, 103 vs; 201 vw, 203 vs; 111 vs, 113 w. Similarly in IB and IIA sets where only *k* varies by 2 have the same structure factor; the observed intensities consistently follow this relation through Table I. IB alone has the too low oxygen–oxygen distance 2.84 Å., depending only on *a* and the side of the nitrate triangle; also IIA is more consistent with the abnormal intensity decline of reflections (*h*00) than IB. Finally IIA alone has the nitrate planes perpendicular to *b*. It was selected and the coördinates rewritten.

Position, V_h^{13}	$k + l$ even	$k + l$ odd
Nh (*b*) $z\,{}^1/_2 0, \bar{z}\,0\,{}^1/_2$	$\pm 2F \cos h2\pi z$ (plus for *l* even)	$\pm 2F \sin h2\pi z$ (plus for *l* odd)
No (*a*) $x00, \bar{x}\,{}^1/_2\,{}^1/_2$	$2F \cos h2\pi x$	$2F \sin h2\pi x$
O (*a*) $y00, \bar{y}\,{}^1/_2\,{}^1/_2$	$2F \cos h2\pi y$	$2F \sin h2\pi y$
O (*f*) $v0u, \bar{v}\,{}^1/_2\,{}^1/_2 + u$ $v0\bar{u}, \bar{v}\,{}^1/_2\,{}^1/_2 - u$	$4F \cos l2\pi u, \cos h2\pi v$	$4F \cos l2\pi u, \sin h2\pi v$

Choice of Parameters.—In calculating structure factors *F* curves for ammonium,[5] nitrogen and oxygen[6] were used. Since the structure factor

[3] D. A. Edwards, *Z. Krist.*, **80**, 154 (1931).

[4] W. L. Bragg, *Proc. Roy. Soc.* (London), **A105**, 370 (1924); **A106**, 346 (1924).

[5] R. W. G. Wyckoff, "The Structure of Crystals," 1931.

[6] R. W. James and G. W. Brindley, *Z. Krist.*, **78**, 470 (1931).

for reflections $(0kl)$ depends only on u, their observed intensities offer a check on this parameter, $2cu$ being one side of the nitrate triangle; the value cited showed satisfactory agreement and was retained. It makes the shortest oxygen–oxygen distance independent of x 3.26 Å. Assuming the nitrate triangles are equilateral, only x and z now remain independently

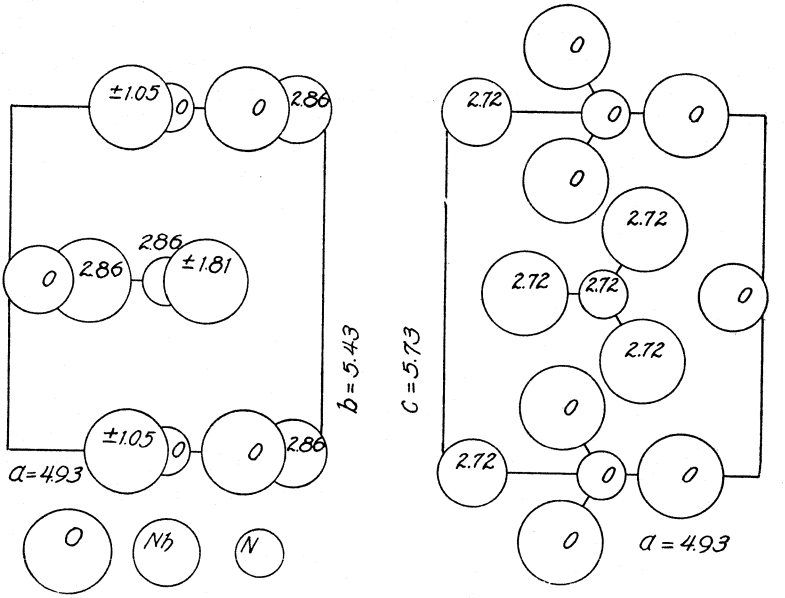


Fig. 1.—Unit cell of ammonium nitrate projected on (001) and (010). The height of each atom is indicated in Ångström units.

variable. The value of x was estimated from the intensities of Laue reflections at large sin ϑ/λ where F_{Nh} is one-third or less of F_O or F_{No}, and z follows from the intensities of powder and oscillation reflections. The structure factors (F^2) of Table I are calculated for the tabulated values

	Parameters			Distances
u	66°	0.183	1.05 Å.	Nh–No: 3.36, 3.48
x	180	.500	2.47	O–O: 3.08, 3.26, 3.33
y	−90	.750	3.70	Each Nh: 2.96 (two oxygen atoms), 2.96 (two atoms)
v	135	.375	1.85	3.18 (two atoms), 3.21 (two atoms)
z	35	.097	0.48	3.22 (four atoms), average of 12 = 3.13

of the parameters; the disagreements with observed intensities are unsystematic and are not considered prohibitive. The calculated distances are similar to those prevailing in like substances except that the first oxygen–oxygen distance is about 3% below the minimum observed and predicted by Zachariasen.[7]

[7] W. H. Zachariasen, *Z. Krist.*, **80**, 137 (1931).

TABLE I

OBSERVED INTENSITIES OF REFLECTIONS FROM AMMONIUM NITRATE

hkl	sin ϑ/λ	F^2	Intensity Osc.	Intensity Laue	hkl	sin ϑ/λ	F^2	Intensity Osc.	Intensity Laue
020	0.184	665	vs	vs*	033	0.380	0	O	
040	.368	166	s		053	.530	0.2	O	
060	.552	66	m		004	.350	41	s	
011	.127	58	vs	s*	024	.394	32	s	
031	.290	36	s	m*	044	.507	18	m	
051	.468	22	m	m	015	.445	45	s	m
002	.175	54	vs	m*	035	.516	37	m	
022	.254	22	s	m*	006	.524	71	m	
042	.407	8.3	m		026	.554	61	m	
013	.277	30	m		017	.616	7.5		O
100	.101	47	vs	s*	110	.137	2.6	s	O*
120	.210	27	vs	m*	130	.294	0	w	O*
140	.382	19	m		101	.134	2.4	O	O*
111	.162	139	vs	vs*	121	.228	0.4	O	O*
131	.307	42	s	vs	141	.392	0	O	O
151	.479	17	m	s	112	.222	162	vs	
102	.202	61	vs		132	.342	60	s	
122	.273	25	s		152	.502	22	m	s
142	.419	3.6	w	m	172	.674	11		w
162	.587	0.3		O	103	.279	60	vs	m*
113	.294	0.6	w	O*	123	.334	43	s	m*
133	.392	0.1	vw	m	143	.462	22	m	s
153	.539	0	O	w	114	.375	21	s	s
104	.363	0.2	O	O	134	.456	12	m	s
124	.407	0	O	w	154	.586	6.6		m
144	.517	0.4	O	w	105	.448	2	O	O
115	.457	35	s	s	125	.484	1.5	O	O
135	.526	25	m	s	145	.580	0.6		O
155	.641	17		w	210	.222	220	vs	
200	.203	2.3	m		230	.342	75	s	
220	.274	1.0	w		250	.502	28	w	
240	.420	0	vw		270	.674	11		w
211	.239	18	s	w*	201	.221	0.2	vw	O*
231	.353	4	w		221	.288	0	O	O*
251	.509	0.4	O	O	241	.429	0.3	O	O
202	.268	1.3	O	O*	212	.283	5.2	m	O*
222	.324	0.5	O		232	.384	4	w	
242	.455	0	O		252	.531	3.2	O	O
213	.344	28	m	s	203	.331	82	vs	
233	.431	1.4	w		223	.379	55	s	
253	.566	0.2		O	243	.495	27	m	
204	.404	0	w		263	.644	13		m
224	.444	0	w		214	.414	1.2	w	w
244	.546	0	O		234	.489	0.5	w	
215	.490	0.6	O	O	205	.481	7	vw	
235	.554	0.2		O	225	.515	6.8		w
300	.304	6.9	O		310	.318	36	s	

TABLE I (*Concluded*)

hkl	$\frac{\sin\vartheta}{\lambda}$	F^2	Intensity Osc.	Intensity Laue	*hkl*	$\frac{\sin\vartheta}{\lambda}$	F^2	Intensity Osc.	Intensity Laue
320	0.356	3.6	O		330	0.411	21	m	
340	.477	0.9	O		301	.317	70	s	s
311	.330	0.6	m	m	321	.366	45	s	vs
331	.420	0	w	m	312	.363	4.3	m	s
302	.350	30	s		332	.446	1.6	w	m
322	.396	25	s		303	.401	0.7	vw	
313	.412	25	s	s	323	.442	0.4	w	
333	.487	19	m		314	.471	0.5	O	w
304	.463	6.5	m		334	.539	0.7	O	
324	.498	6	m	s	410	.416	1.3	vw	m
400	.406	4.5	O		430	.491	0.6	O	
420	.445	2.8	O		401	.414	1.3	m	s
411	.424	13	m	s	421	.454	0.8	m	m
431	.498	9	m	m	412	.451	0.8	O	w
402	.441	40	s		432	.521	0.5		O
422	.478	36	m		403	.483	0.6	m	
413	.491	81	s	s	423	.516	0.5	w	m
433	.556	61		s	510	.515	26	m	s
500	.507	0	O		530	.577	11	m	
520	.539	0		O	501	.515	10	m	s
511	.523	0.2	w	w	521	.546	9	w	m
531	.584	0		O	512	.544	0	w	m
502	.536	21	m	m	532	.603	0		w
522	.567	18	w	m	503	.570	0.5	O	O
513	.578	13	w	w	523	.600	0.4		O

* Powder reflection.

Discussion.—A marked feature of the structures of lithium, sodium and potassium nitrates is the separation into alternate layers of metal ions and nitrate groups which lie parallel to the nitrate planes. In the present form of the ammonium compound this characteristic is absent, although there is a suggestion of such layering in the direction of the *a*-axis perpendicular to the nitrate planes. This structure may be considered as related to the cesium chloride type if the nitrate groups are taken as units.

I am grateful to Professor Albert Sauveur for the use of x-ray apparatus.

Summary

A complete structure is proposed for rhombic ammonium nitrate in the space group V_h^{13}. As in some other univalent nitrates, the strong double refraction is probably to be explained by the arrangement of the nitrate groups in parallel planes.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. VIII. COMPLEX DIPOLES AND LONG-CHAIN MOLECULES

BY C. P. SMYTH AND W. S. WALLS

RECEIVED JANUARY 30, 1932 PUBLISHED JUNE 6, 1932

Previous papers have treated the moments of the ethyl esters of dicarboxylic acids,[1] the glycols,[2] and the polymethylene bromides[3] and the results obtained in these papers have been graphically examined by Ebert and Höjendahl,[4] whose conclusions are in essential agreement with those drawn in the original papers. It has seemed desirable to measure tetramethylene bromide for comparison with the bromides containing three-carbon and five-carbon chains and to measure in benzene solution the other long-chain bromides which were previously measured in heptane, thus obtaining data under identical conditions for careful comparison. Other more or less similar molecules have been studied and the data will be subjected to a quantitative treatment in an attempt to gain further information concerning the resolution of two or more moments in a molecule and the shape of a long carbon chain.

Resolution of Moments

In the ethylene halide molecules, rotation around the C–C bond makes it possible for the dipoles to occupy different positions relative to one another, the positions not being equally probable, however, because of the mutual potential energies of the dipoles and of steric effects. This problem has been treated in a previous paper.[5] Since, in more complex molecules, it becomes even more difficult to calculate the potential energy and its effect upon the oscillation of the dipoles, we shall, in these calculations, disregard the mutual potential energies of the dipoles, their variable inductive effects upon one another, and steric effects, and assume that, in rotation about any single bond, all positions are equally probable. Cases in which the results of these calculations may be thrown into serious error by the neglected potential energy may then be examined qualitatively. With the assistance of Dr. Henry Eyring, each type of molecule was treated separately in order to derive an equation for its moment, but, finally, the matrix algebra was employed by Dr. Eyring[6] to derive a general equation, from which the equations for the different types could be derived. The equations for the moments of the particular molecules studied here are

[1] Smyth and Walls, THIS JOURNAL, **53**, 527 (1931).
[2] Smyth and Walls, *ibid.*, **53**, 2115 (1931).
[3] Smyth and Kamerling, *ibid.*, **53**, 2988 (1931).
[4] Ebert and Höjendahl, *Z. physik. Chem.*, [B] **15**, 74 (1931).
[5] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).
[6] Eyring, *Phys. Rev.*, **38**, 746 (1932).

given below, the bond moments being represented by m, the carbon valence angle by θ, taken as 110°,[7] and the oxygen valence angle by α, also taken as 110° in the calculations for Table IV

$Br(CH_2)_nBr$ m_1 = C—Br, $\mu = m_1\sqrt{2 - 2(-\cos\theta)^n}$

$CH_2BrCHBrCH_2Br$ m_1 = C—Br, $\mu = m_1\sqrt{3 + 4\cos^2\theta + 2\cos^3\theta}$

$HO(CH_2)_2OH$ m_2 = C—O, m_3 = H—O,

$$\mu = \sqrt{2(m_2^2 + m_3^2 - m_2^2\cos^2\theta - m_3^2\cos^2\alpha\cos^2\theta + 2m_2m_3\cos\alpha\sin^2\theta)}$$

$Cl(CH_2)_2OH$ m_1 = C—Cl, m_2 = C—O, m_3 = H—O,

$$\mu = \sqrt{m_1^2 + m_2^2 + m_3^2 - 2m_1m_2\cos^2\theta + 2m_2m_3\cos\alpha - 2m_1m_3\cos\alpha\cos^2\theta}$$

$Cl(CH_2)_3OH$, or $Br(CH_2)_3OH$ m_1 = C—Cl or C—Br, m_2 = C—O, m_3 = H—O,

$$\mu = \sqrt{m_1^2 + m_2^2 + m_3^2 + 2m_1m_2\cos^3\theta + 2m_2m_3\cos\alpha + 2m_1m_3\cos\alpha\cos^3\theta}$$

$(CH_2XCH_2)_2O$ m_1 = C—X, m_3 = resultant of two C—O moments, which acts in the line bisecting α, $\mu = \sqrt{2m_1^2 + m_3^2 + 2m_1^2\cos^5\theta - 4m_1m_3\cos^2\theta\cos\theta/2}$

Preparation of Materials

Heptane, benzene,[8] trimethylene bromide[3] and dioxane,[2] were purified as in earlier work. The dioxane was kept standing over sodium and was freshly distilled just before using. Its physical constants depended somewhat upon the duration of the drying and were newly determined for each lot used.

Tetramethylene Bromide.—Furfuran obtained from the Miner Laboratories, Chicago, was converted into tetrahydrofuran under the direction of Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company by catalytic reduction in butyl alcohol solution. This material, having been purified by fractional distillation, was treated with three times the theoretical amount of 48% hydrobromic acid. After heating at 100–105° for seven to eight hours, the reaction mixture was very slowly distilled and the heavy layer of tetramethylene bromide in the distillate was separated, the yield being 70% of the theoretical. Experiments carried out at a slightly higher temperature with a more rapid distillation of the product led to decomposition and a decreased yield. As suggested by Dr. J. R. Johnson in a communication to Dr. Carothers, a little pure ethyl bromide was added as a solvent to prevent the formation of troublesome emulsions, and the mixed bromides were washed with ice water, with cold strong sulfuric acid, with water, twice with dilute sodium bicarbonate solution, and several times with water. The product was dried with anhydrous calcium chloride, the ethyl bromide distilled off with a steam-bath and the residual tetramethylene bromide fractionally distilled under reduced pressure. The fraction distilling at 85–85.5° (18 mm.) was redistilled; b. p. 81° (15 mm.).

Pentamethylene Bromide.—Material kindly loaned by Dr. Carothers was dried with anhydrous calcium chloride and fractionally distilled under reduced pressure; b. p. 106.9–107.4° (24 mm.).

Decamethylene Bromide.—Material loaned by Dr. Carothers was distilled under reduced pressure; b. p. 182–183° (22 mm.). The material was further purified by three fractional crystallizations; m. p. 23.5°.

1,2,3-Tribromopropane.—Material obtained from the Eastman Kodak Company (b. p. 143–145°, 80 mm.) was dried with anhydrous calcium chloride and fractionally distilled under reduced pressure; b. p. 96.0–96.2° (13 mm.).

[7] Smyth and Walls, THIS JOURNAL, **54**, 1854 (1932).

[8] Ref. 7, p. 1857.

Ethylene Chlorohydrin.—Material from the Dow Chemical Company was twice fractionally distilled; b. p. 128.1–128.2° (752 mm.).

Trimethylene Chlorohydrin.—Material from the Eastman Kodak Company was twice fractionally distilled under reduced pressure; b. p. 66.0–66.2° (16 mm.).

Trimethylene Bromohydrin.—Material from the Eastman Kodak Company was fractionally distilled under reduced pressure three times; b. p. 77–78° (16 mm.).

β,β′-Dichloroethyl Ether.—Material loaned by Dr. W. L. Ruigh of Merck and Co., Inc. (a fraction of some material obtained from the Carbide and Chemical Company) was dried with anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 75.0 ±0.1° (20 mm.).

β,β′-Diiodoethyl Ether.—Material loaned by Dr. Ruigh, which had become slightly colored from standing, was twice shaken with "Darco" to remove coloration, then shaken with mercury, dried over anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 102.3 ±0.1° at 4 mm., distilling at the rate of four drops in three seconds with the bath at 130°.

The densities and refractive indices given in Table II may be taken as criteria of purity.

Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the non-polar were measured with the apparatus and methods previously employed,[1] a wave length of 1000 meters being used in the dielectric constant determinations. In Table I the first column gives the mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ, the densities d of the solutions and the polarizations P_2 of the polar substance. The values of the moment in Table III were obtained as in previous papers.[1]

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Benzene–Trimethylene Bromide			
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01145	2.340	2.284	.8881	.8610	109.7	105.4
.01591	2.367	2.305	.8938	.8665	110.9	104.1
.01826	2.380	2.317	.8965	.8689	111.0	105.6
.03719	2.490	2.414	.9203	.8924	110.6	105.0
.04701	2.548	2.464	.9324	.9042	110.5	104.6
.07254	2.696	2.597	.9639	.9352	108.5	103.6
.11556	2.948	2.824	1.0166	.9869	105.3	101.4
			Benzene–Tetramethylene Bromide			
0.01344	2.354	2.297	0.8905	0.8631	117.5	114.6
.02002	2.392	2.332	.8986	.8711	117.6	114.7
.02546	2.424	2.360	.9055	.8780	117.4	114.0
.04549	2.542	2.465	.9301	.9022	116.8	112.7
.09057	2.813	2.712	.9846	.9558	114.6	111.2
.11226	2.944	2.828	1.0104	.9812	113.3	109.9

TABLE I (*Continued*)

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
Heptane–Tetramethylene Bromide						
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.03680	2.035	1.992	.7137	.6913	114.5	113.4
.05889	2.107	2.058	.7346	.7117	113.7	111.9
.07512	2.163	2.110	.7496	.7265	114.2	112.2
.11276	2.296	2.233	.7859	.7618	113.2	111.4
Benzene–Pentamethylene Bromide						
0.00862	2.337	2.280	0.8843	0.8573	140.4	133.5
.01416	2.376	2.315	.8913	.8641	140.4	134.1
.02387	2.447	2.377	.9033	.8758	141.5	134.9
.03153	2.504	2.431	.9126	.8851	141.8	136.9
.04047	2.571	2.491	.9234	.8959	141.8	136.5
.04621	2.612	2.528	.9304	.9026	141.0	135.9
.07320	2.814	2.709	.9634	.9352	138.7	133.9
.10953	3.071	2.941	1.0039	.9755	134.8	130.6
Benzene–Decamethylene Bromide						
0.01580	2.417	2.353	0.8920	0.8650	194.4	187.6
.02617	2.510	2.434	.9036	.8766	194.4	186.5
.03814	2.615	2.528	.9166	.8896	193.2	185.7
.05744	2.776	2.673	.9365	.9095	189.8	183.1
.07771	2.939	2.821	.9564	.9294	186.8	180.8
Benzene–1,2,3-Tribromopropane						
0.01262	2.325	2.270	0.8988	0.8713	89.3	87.0
.02432	2.369	2.312	.9219	.8940	89.2	87.6
.04719	2.457	2.391	.9666	.9380	89.2	86.7
.07055	2.547	2.472	1.0123	.9827	88.5	85.9
.08908	2.618	2.538	1.0474	1.0174	88.2	85.8
Heptane–1,2,3-Tribromopropane						
0.03737	1.996	1.954	0.7311	0.7082	84.4	82.5
.06351	2.053	2.006	.7680	.7441	84.5	82.6
.11246	2.165	2.108	.8375	.8124	84.8	82.4
.15218	2.265	2.197	.8956	.8693	85.1	82.3
Benzene–Ethylene Chlorohydrin						
0.01247	2.338	2.280	0.8764	0.8492	90.8	86.1
.01776	2.366	2.306	.8776	.8505	92.0	88.1
.03051	2.438	2.367	.8806	.8533	94.5	89.0
.03193	2.445	2.371	.8808	.8536	94.3	89.1
.04086	2.494	2.417	.8830	.8559	93.7	88.7
.06225	2.628	2.534	.8881	.8607	95.6	90.7
.08002	2.740	2.628	.8924	.8651	95.5	90.0
.08288	2.761	2.647	.8933	.8659	95.7	90.4
.18405	3.584	3.343	.9193	.8916	96.4	91.1

TABLE I (*Concluded*)

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
1,4-Dioxane (n_D^{20} 1.42310)–Ethylene Chlorohydrin						
0.00000	2.261	2.214	1.0312	1.0027	(25.27	25.30 = P_1)
.01946	2.388	2.329	1.0363	1.0079	106.0	101.4
.03465	2.488	2.418	1.0382	1.0098	105.2	100.6
.05234	2.614	2.531	1.0405	1.0120	105.5	101.2
.05963	2.665	2.579	1.0414	1.0130	105.1	101.1
.08114	2.824	2.718	1.0441	1.0157	104.2	99.9
Benzene–Trimethylene Chlorohydrin						
0.02042	2.414	2.351	0.8781	0.8511	120.7	116.9
.03818	2.538	2.464	.8825	.8555	120.2	116.6
.05889	2.688	2.601	.8872	.8602	118.2	115.1
.08343	2.877	2.769	.8932	.8663	117.1	113.7
.11879	3.161	3.025	.9016	.8748	114.9	111.7
.14638	3.407	3.238	.9086	.8817	113.7	110.3
1,4-Dioxane (n_D^{20} 1.42320; n_D^{25} 1.42085)–Trimethylene Chlorohydrin						
0.00000	2.217	2.176	1.0311	1.0026	(24.65	24.74 = P_1)
.02758	2.422	2.363	1.0303	1.0016	129.5	125.5
.04378	2.551	2.478	1.0316	1.0032	128.4	123.6
.07720	2.831	2.724	1.0346	1.0064	125.5	120.3
.08517	2.894	2.783	1.0353	1.0073	124.1	119.3
.12558	3.247	3.094	1.0387	1.0110	120.1	115.5
Benzene–Trimethylene Bromohydrin						
0.01631	2.385	2.326	0.8847	0.8578	121.1	117.5
.02979	2.479	2.410	.8938	.8666	121.7	117.7
.06778	2.756	2.656	.9204	.8928	119.5	115.0
.07527	2.812	2.708	.9255	.8980	118.9	114.7
.08427	2.882	2.769	.9319	.9042	118.4	114.1
Benzene–β,β'-Dichloroethyl Ether						
0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.01595	2.425	2.354	.8805	.8535	168.4	157.1
.02437	2.507	2.424	.8842	.8572	168.3	156.4
.03968	2.656	2.555	.8909	.8639	166.1	155.7
.05689	2.836	2.703	.8984	.8714	165.2	153.8
.08033	3.083	2.913	.9086	.8815	162.4	151.7
.09818	3.283	3.077	.9161	.8890	160.8	150.1
.12253	3.555	3.307	.9263	.8991	157.7	147.8
Benzene–β,β'-Diiodoethyl Ether						
0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.01287	2.372	2.311	.9030	.8753	148.7	141.7
.02350	2.451	2.381	.9266	.8986	148.0	140.7
.03131	2.509	2.432	.9441	.9159	146.8	139.4
.04295	2.595	2.507	.9694	.9407	145.4	138.2
.04999	2.648	2.555	.9850	.9556	144.5	138.1
.05509	2.683	2.587	.9956	.9662	143.6	137.4

TABLE II

REFRACTIVE INDICES AND DENSITIES OF THE PURE LIQUIDS

	d_4^{25}	d_4^{50}	n_D^{20}	n_D^{25}
Trimethylene bromide	1.9701	1.9250	1.52319	1.52090
Tetramethylene bromide	1.8177	1.7786	1.51908	1.51685
Pentamethylene bromide	1.6927	1.6574	1.51255	1.51028
Decamethylene bromide	1.349	1.3223	.....	1.4914
1,2,3-Tribromopropane	2.4076	2.3586	1.58594	1.58349
Ethylene chlorohydrin	1.1947	1.1671	1.44208	1.44012
Trimethylene chlorohydrin	1.1260	1.1022	1.44586	1.44418
β,β'-Dichloroethyl ether	1.2139	1.1844	1.45750	1.45534
β,β'-Diiodoethyl ether	2.3317	2.2855	.....	.....

TABLE III

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	Solvent	MR_D	$P_\infty - MR_D$ 25°	$P_\infty - MR_D$ 50°	$\mu \times 10^{18}$ 25°	$\mu \times 10^{18}$ 50°
Trimethylene bromide	Benzene	31.20	81.1	75.4	1.97	1.98
Tetramethylene bromide	Benzene	35.93	83.0	79.3	2.00	2.03
Tetramethylene bromide	Heptane		79.8	77.9	1.96	2.01
Pentamethylene bromide	Benzene	40.64	105.1	99.7	2.25	2.28
Decamethylene bromide	Benzene	63.9[a]	134.3	125.7	2.54	2.56
1,2,3-Tribromopropane	Benzene	39.01	51.1	48.7	1.57	1.59
1,2,3-Tribromopropane	Heptane		45.3	43.6	1.48	1.51
Ethylene chlorohydrin	Benzene	17.76	73.7	68.7	1.88	1.89
Ethylene chlorohydrin	1,4-Dioxane		88.7	83.9	2.07	2.09
Trimethylene chlorohydrin	Benzene	22.31	100.2	96.2	2.19	2.24
Trimethylene chlorohydrin	1,4-Dioxane		110.4	105.7	2.30	2.35
Trimethylene bromohydrin	Benzene	25.2[a]	98.1	93.8	2.17	2.21
β,β'-Dichloroethyl ether	Benzene	31.98	138.5	127.0	2.58	2.57
β,β'-Diiodoethyl ether	Benzene	47.39[a]	103.7	95.6	2.23	2.23

[a] Calculated from measurements upon solutions.

Discussion of Results

The values for the moments of trimethylene bromide, pentamethylene bromide and decamethylene bromide are 0.2×10^{-18} lower than the corresponding values previously found in heptane solution.[3] As the value given in Table III for tetramethylene bromide in benzene is higher than that in heptane by an amount too small to be significant and as the values for the ethylene halides are decidedly higher in benzene than in heptane, the reason for the discrepancy is not apparent. The bromides used were the same materials employed in the previous measurements, and had been subjected to further purification without appreciable alteration of the refractive indices. As the present measurements form part of a long series carried out with great care in the same way, they will be regarded as correct. In any event, the small difference does not materially affect the conclusions to be drawn.

The value for ethylene chlorohydrin is 0.20×10^{-18} higher in dioxane

than in benzene solution, while the trimethylene compound is 0.11×10^{-18} higher. As dioxane may introduce complications through compound formation with the solute, it appears probable that the values obtained in benzene are the more accurate, the possible error in the dioxane values decreasing with increasing separation of the dipoles. This suggests that the values obtained for the two- and three-carbon glycols in dioxane solution[2] may be from $0.1–0.3 \times 10^{-18}$ high, which would make the moments of ethylene and propylene glycol about 2.0×10^{-18}. The values for the six- and ten-carbon glycols should be but little low, as the two hydroxyl groups should be almost independent of one another at these distances and it was shown that butyl alcohol had almost the same moment in dioxane as in benzene solution. However, it appears consistent to lower the former values for the three-, six- and ten-carbon glycols by 0.2×10^{-18}.

In the quantitative treatment of these moments, the results of which are given in Table IV, a value of 1.5×10^{-18} is assigned to the C–Br moments in 1,2,3-tribromopropane, as in ethylene bromide, 1.7×10^{-18} to the C–Br moments in trimethylene bromide, and 1.9×10^{-18} in the three longer molecules.[3] The difference in the values used is the result of a rough approximation made in an attempt to take care of the small effects of induction upon the carbon chain and of the possible C–H moments. The lumping of these effects in a single moment in the C–Br line may introduce an error of as much as 0.2×10^{-18}, but in the four-, five- and ten-carbon molecules, at least, the error should be practically the same. The other moments used in Table IV are taken from data previously summarized.[9] The possible error resulting from the assumption that the

TABLE IV

CALCULATED AND OBSERVED VALUES OF MOMENTS ($\times 10^{18}$)

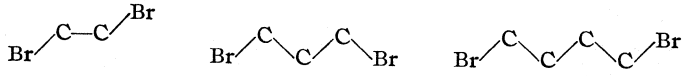
	m_1	m_2	m_3	μ calcd.	μ obs.
$Br(CH_2)_2Br$	1.5			1.99	0.8–1.05
$Br(CH_2)_3Br$	1.7			2.36	1.98
$Br(CH_2)_4Br$	1.9			2.67	2.01
$Br(CH_2)_5Br$	1.9			2.68	2.28
$Br(CH_2)_{10}Br$	1.9			2.69	2.56
$CH_2BrCHBrCH_2Br$	1.5			2.36	1.58
CH_2OHCH_2OH		0.7	1.6	2.1	2.0
$CH_3CHOHCH_2OH$		.7	1.6	2.1	2.0
$HO(CH_2)_3OH$		.7	1.6	2.1	2.3
$HO(CH_2)_6OH$		.7	1.6	2.1	2.3
$HO(CH_2)_{10}OH$		.7	1.6	2.1	2.3
CH_2ClCH_2OH	1.9	7	1 6	2.41	1.89
$CH_2ClCH_2CH_2OH$	1.9	.7	1.6	2.42	2.24
$CH_2BrCH_2CH_2OH$	1.9	.7	1.6	2.42	2.21
$(CH_2ClCH_2)_2O$	1.9		1.14	2.94	2.57
$(CH_2ICH_2)_2O$	1.6		1.14	2.43	2.23

[9] Eucken and Meyer, *Physik. Z.*, **30**, 387 (1929); Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931.

oxygen valence angle is 110° is no greater than that in the values for the C–O and H–O moments.

The moment of the ethylene bromide molecule is far lower than the calculated value because the two C–Br dipoles lower each other's moments by greater inductive action as they approach more closely the *cis* position, the position of maximum resultant moment, because the mutual potential energy of the dipoles tends to make this *cis* position least probable,[5] and because of the interatomic forces characterized by the term "steric effect." This steric effect is so complicated by the necessity of considering the interaction of bromine with bromine, bromine with hydrogen, and hydrogen with hydrogen, that the quantitative treatment of all the combined effects requires a separate communication. As is to be expected, these effects diminish with increasing length of the carbon chain until, in decamethylene bromide, the difference between the observed and the calculated values is less than the probable error, and the increase of the moment with rising temperature has disappeared. Calculation shows that if pentamethylene bromide had an extended rod-like molecule, the potential energy between the two C–Br dipoles would still not be wholly negligible in comparison with kT, as it is in an extended decamethylene bromide molecule. If there is sufficient freedom of rotation about the C–C bonds to give a great variety of forms to the molecules, those forms in which the dipoles point more or less in the same direction should be less probable in the shorter molecules and the moments should be smaller than the calculated values, the difference decreasing with increasing length of the chain. The observed and calculated values of decamethylene bromide are indistinguishable from that which would result from a completely random orientation of the two dipoles relative to each other. This theory of more or less free rotation about the C–C bonds explains all the results for the polymethylene bromides except the close proximity of the value for tetramethylene bromide to that of trimethylene bromide.

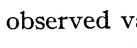
From preliminary considerations it appears that a hydrocarbon chain is in a position of minimum potential energy when in the zigzag form indicated for it in solids, in films, and even in liquids.[10] For the polymethylene bromides, this would give structures somewhat as follows:



etc. The C-Br dipoles would not necessarily cancel each other in the even-numbered chains as shown above, but there would certainly be a sharp alternation of moment in going up the series. If there is freedom of rotation only about the end C–C bonds, where the inhibition of rotation should be less than in the case of a bond with another C–C on each side, it is evident

[10] Gane and Ingold, *J. Chem. Soc.*, 2153 (1931); Ingold, *ibid.*, 2170 (1931).

that the even-numbered molecules should have moments equal to the value 2.52×10^{-18} calculated for the ethylene compound and the odd-numbered molecules values equal to that for the trimethylene compound, 2.63×10^{-18}, the C–Br moment being taken as 1.9×10^{-18}. The differences between these values and those calculated for the longer molecules on the assumption of free rotation about the C–C bond are not sufficient to permit of distinction between the fixed and the variable structures. However, the fact that a higher moment is indicated for the odd-numbered molecules offers an explanation of the proximity of the moment of tetramethylene bromide to that of trimethylene bromide, while, if there were freedom of rotation about the C–C bonds, it should be closer to the value for pentamethylene bromide. The moment calculated for 1,2,3-tribromopropane is much higher than the observed values in Table IV because of these same effects.

The reason that the observed moments of ethylene and propylene glycol do not lie far below the calculated as in the case of ethylene bromide is apparent when the structure is considered. If, as an extreme case, the potential energy between the dipoles caused the hydroxyls to occupy a *trans* position,  , a position in which ethylene bromide would have zero moment, the two C–O moments would cancel each other, but the two H–O moments would rotate around the extensions of the C–O lines in such a way that their mutual potential energies would lower the resultant moment only a little below the calculated value in Table IV. Evidently, little lowering of the moment below the calculated value is to be expected unless there is a tendency toward ring formation in the longer molecules and the uniformity of the observed values indicates the absence of such formation. It is not surprising, therefore, to find in the longer glycols the only case in Table IV in which the observed moments are higher than the calculated, the difference very possibly arising from the use of too low values for the C–O moment, if not for the H–O. If the not unreasonable value 1.1×10^{-18} is used for the C–O moment, the calculated value for the glycols is 2.25×10^{-18}. As is to be expected, the behavior of the chloro- and bromohydrins is intermediate between that of the glycols and that of the polymethylene halides. The trimethylene compounds have moments not far below the calculated and the same is true of the β,β'-dihalogenated ethers.

It has not seemed worth while to calculate the moments of the diethyl esters of the dicarboxylic acids because each half of the molecule contains three dipoles, one C=O and two C–O, the moments of which, as well as the angles, have to be estimated, and the mutual inductive action of which may be considerable because of the large size of the C=O moment. Evidently, the situation in these molecules is somewhat analogous to that in the

glycols. The large mutual potential energies of the dipoles have little effect upon the resultant moment, so that the ethyl oxalate molecule has a moment practically the same as those of the very long molecules. It is only in the diethyl succinate molecule, where there is good reason to believe in the formation of a ring, that any considerable difference in moment occurs. The results justify the conclusion originally drawn that the long chains do not bend around upon themselves to form ring structures.

The writers wish to thank Dr. Wallace H. Carothers for the loan of materials and for assistance and advice in preparation and purification, and Dr. Henry Eyring for his assistance in the derivation of the equations.

Summary

Equations have been derived for the calculation of the electric moments of molecules of various lengths, containing two, three and four dipoles which may move relatively to one another.

The moments of four polymethylene bromides, 1,2,3-tribromopropane, two chlorohydrins, a bromohydrin and two dihalogenated ethers have been determined and the results, together with previously measured values for the glycols, now slightly revised, are compared with the values calculated by means of the equations. It is shown that dipoles not far apart on a carbon chain affect one another's positions in such a way as to diminish the resultant moment of the molecule. The results for the liquids may be explained by supposing that free rotation about the C–C bonds gives a great variety of forms to long-chain molecules, some of which are excluded because of high mutual potential energies of the dipoles, but a more satisfactory explanation is given by the supposition of an extended zigzag structure of the carbon chain with complete freedom of rotation only at the ends of the chain. In these solutions, any considerable bending around of the polar molecules to form ring structures is excluded in most cases.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF LEAD CHLORIDE AND LEAD BROMIDE

BY A. WACHTER[1]

RECEIVED FEBRUARY 2, 1932 PUBLISHED JUNE 6, 1932

The investigation described in this paper represents an extension of the experimental methods described in a previous paper[2] for the determination of the thermodynamic properties of solid salts and their solid solutions by a study of the e. m. f. of cells containing solid electrolytes. Such measurements give accurate data concerning activities over a large temperature range and are of great interest in connection with the general theories of solution and with the theories concerning the structure and properties of solid solutions. In the previous investigation a study was made of solid solutions of sodium chloride in silver chloride. In the present work solid solutions of lead bromide in lead chloride were studied. This system is especially suitable for the application of these experimental methods since the freezing point is a linear function of the composition,[3] indicating the existence of a continuous series of solid solutions and the absence of either compound formation or a separation into two or more phases. The close proximity of the liquidus and solidus branches of the equilibrium diagram is of considerable assistance in the rapid attainment of a homogeneous solution when the molten mixture is cooled and annealed.

Experimental Part

The cell studied in this research can be represented by $Pb/PbCl_2$, $PbBr_2/AgCl$, Ag, where all the materials are solid and lead bromide is in solid solution with lead chloride. The cell reaction is

$$Pb + 2AgCl = PbCl_{2(soln.)} + 2Ag$$

The preparation and purification of the substances employed in the cells as well as the experimental procedure are essentially the same as those described for the silver chloride–sodium chloride system,[2] with the following exceptions. Lead bromide was purified by bubbling dry hydrogen bromide, which was obtained by passing a mixture of hydrogen and bromine over a heated platinum catalyst, through the molten salt. The cell was prepared by pouring a molten solution of the lead salts into a Pyrex glass U-tube until the bend was completely filled. Before the melt solidified a silver wire was inserted into one arm of the tube about 1 cm. below the surface of the melt. It was then annealed at a temperature just below its melting point for about twenty-four hours. After slowly cooling to room

[1] National Research Fellow in Chemistry.

[2] Wachter, THIS JOURNAL, **54**, 919 (1932).

[3] Monkmeyer, *Neues Jahrb.*, **22**, 1 (1906).

temperature a 5-mm. layer of molten silver chloride was poured into the arm containing the silver wire and a layer of lead poured into the other arm. A tungsten wire made electrical contact to the lead electrode. The cells were then placed in a high temperature bath which could be varied from 200 to 300°. This bath was made up of a half liter wide-mouthed Pyrex Dewar flask filled with a low melting Wood's metal alloy. It was heated by means of an immersion resistance unit and stirred with a glass spiral.

TABLE I

E. M. F. IN VOLTS OF CELLS CONTAINING LEAD CHLORIDE OF VARIOUS MOLE FRACTIONS, N_1, DILUTED WITH LEAD BROMIDE

t, °C.	E. m. f.
$N_1 = 1.000$	
201.5	0.4568
203.7	.4564
208.5	.4549
210.5	.4548
213.6	.4539
218.0	.4526
223.0	.4512
225.3	.4512
232.3	.4487
234.1	.4486
238.9	.4474
243.2	.4468
245.9	.4462
250.4	.4454
253.7	.4446
261.6	.4424
269.9	.4408
272.6	.4400
279.5	.4383
284.6	.4373
287.7	.4366
289.3	.4357
295.4	.4350
298.5	.4341
$N_1 = 0.892$	
210.7	0.4057
218.9	.4047
223.7	.4039
230.9	.4021
237.4	.4011
247.8	.3987
256.9	.3971
264.8	.3955
268.9	.3948

t, °C.	E. m. f.
$N_1 = 0.781$	
210.1	0.3829
225.9	.3792
237.2	.3776
262.8	.3723
266.2	.3720
270.4	.3704
285.6	.3673
292.9	.3658
$N_1 = 0.752$	
211.3	0.3794
213.3	.3788
264.9	.3688
275.3	.3669
286.0	.3648
287.5	.3644
290.6	.3636
$N_1 = 0.680$	
220.4	0.3684
230.0	.3668
237.1	.3655
245.1	.3641
247.7	.3635
256.0	.3620
264.4	.3603
271.8	.3586
281.7	.3576
287.0	.3560
287.9	.3548
290.7	.3550

t, °C.	E. m. f.
$N_1 = 0.539$	
220.8	0.3485
230.0	.3464
233.1	.3460
236.8	.3450
244.5	.3436
247.5	.3433
255.4	.3412
258.5	.3403
264.4	.3395
268.7	.3391
271.8	.3378
279.1	.3367
281.7	.3357
288.5	.3344
290.7	.3337
$N_1 = 0.303$	
210.4	0.3286
221.6	.3258
223.5	.3260
226.1	.3254
228.1	.3248
234.9	.3235
237.7	.3227
240.4	.3225
248.4	.3207
259.1	.3184
$N_1 = 0.200$	
210.4	0.3206
223.7	.3178
228.1	.3168
235.2	.3151
237.6	.3145
240.4	.3144
248.7	.3128
258.8	.3101

This construction insured a uniform temperature throughout the system. Within two days equilibrium was attained and potential measurements were made by means of a Leeds and Northrup Type K potentiometer in conjunction with a high sensitivity galvanometer. The composition of the cells was varied from mole fraction 0.200 to 1.000 of lead chloride.

The results of the e. m. f. measurements for eight different compositions are given in Table I and plotted in Fig. 1. The values for pure lead

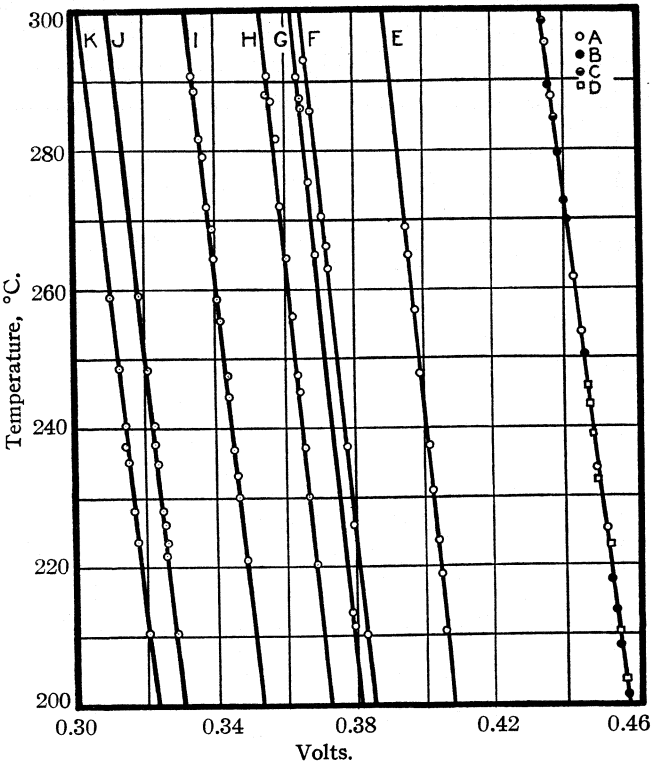


Fig. 1.—Temperature variation of e. m. f. of cells containing different lead chloride–lead bromide solid solutions. Mole fraction of lead chloride in A, B, C and D is 1.000, E is 0.892, F is 0.781, G is 0.752, H is 0.680, I is 0.539, J is 0.303 and K is 0.200.

chloride represent four different cells, indicated in the figure by points of different styles. The average deviation of the points from the straight lines of the plot is less than 0.3 mv. These curves were easily reproduced ascending and descending the temperature scale even after several weeks in the high temperature bath. From a large scale plot of Fig. 1 the e. m. f. at temperatures of 200, 250 and 300° were read off for each solution and plotted against the composition. This is given in Fig. 2.

Discussion of Results

The thermodynamic calculations employing the data obtained for this system were made as described in the previous paper on the silver chloride–sodium chloride system.[2] The results of the calculations are given in Table II and the activities, a_1 and a_2, of both constituents of the solid solutions plotted against the mole fraction, N_1, of lead chloride in Fig. 3. The broken diagonal lines in the figure represent Raoult's law. ΔF is the free energy of the cell reaction; $\Delta\bar{F}_1$, the partial molal free energy of lead chloride; ΔH, the change in heat content of the cell reaction; $\Delta\bar{H}_1$, the partial molal heat content of lead chloride; ΔS, the entropy change of the

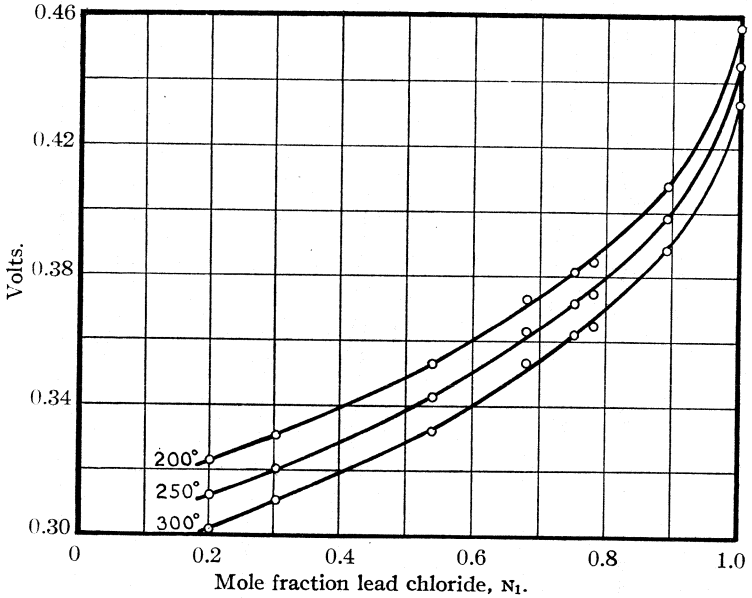


Fig. 2.—Change in e. m. f. of cells upon dilution of lead chloride with lead bromide at 200, 250 and 300°.

cell reaction; $\Delta\bar{S}_1$, the partial molal entropy; and a_1 and a_2, the activity of lead chloride and lead bromide, respectively. The partial molal quantities and the activity of lead chloride in its solutions were calculated taking the pure salt as the standard state. Pure lead bromide was taken as the standard state for lead bromide in the solid solutions.

The activity curves of Fig. 3 are particularly interesting. It is observed that when lead bromide is added to lead chloride an enormous decrease in the activity of the latter occurs. Below mole fraction 0.9 of lead chloride its activity is less than 0.1. This large negative deviation from Raoult's law is most probably ascribable to a very strong tendency toward compound formation. On the other hand, the activity curve for lead bromide

TABLE II

THERMODYNAMIC PROPERTIES OF LEAD CHLORIDE DILUTED WITH LEAD BROMIDE[a]

N_1	$-dEdT$ (mv./deg.)	$-\Delta s$ (cal./deg.)	$\Delta\bar{s}_1$ (cal./deg.)	$-\Delta H$ (cal.)	$-\Delta\bar{H}_1$ (cal.)
1.000	0.234	10.80	0	26200	0
0.900	.199	9.19	1.61	23270	2930
.800	.184	8.49	2.31	21980	4220
.700	.194	8.95	1.85	21490	4710
.600	.197	9.09	1.71	20930	5270
.500	.202	9.32	1.48	20520	5680
.400	.202	9.32	1.48	20070	6130
.300	.200	9.23	1.57	19620	6580
.200	.215	10.2	0.60	19740	6460

200°

N_1	E (volts)	$-\Delta F$ (cal.)	$-\Delta\bar{F}_1$ (cal.)	a_1	a_2
1.000	0.4570	21090	0	1.000	0
0.900	.4099	18920	2170	0.0991	0.000014
.800	.3892	17960	3130	.0359	.00561
.700	.3737	17250	3840	.0168	.0575
.600	.3604	16630	4460	.00873	.195
.500	.3490	16110	4980	.00500	.394
.400	.3393	15660	5430	.00310	.585
.300	.3304	15250	5840	.00200	.724
.200	.3228	14900	6190	.00138	.818

250°

1.000	0.4452	20550	0	1.000	
0.900	.4011	18510	2040	0.141	
.800	.3800	17540	3010	.0554	
.700	.3636	16780	3770	.0268	
.600	.3503	16170	4380	.0148	
.500	.3388	15640	4910	.00891	
.400	.3293	15200	5350	.00584	
.300	.3203	14780	5770	.00392	
.200	.3120	14400	6150	.00271	

300°

1.000	0.4336	20010	0	1.000	
0.900	.3900	18000	2010	0.171	
.800	.3708	17110	2900	.0785	
.700	.3543	16350	3660	.0403	
.600	.3407	15730	4280	.0232	
.500	.3288	15170	4840	.0143	
.400	.3191	14730	5280	.00968	
.300	.3104	14330	5680	.00681	
.200	.3013	13910	6100	.00470	

[a] 1 volt-equivalent = 23,074 cal.

at first shows a small positive deviation when lead chloride is added which, beyond mole fraction 0.4 of lead chloride, rapidly becomes a larger and larger negative deviation. From the large downward pull on the curves in

the region of solid solutions most concentrated in lead chloride, one would suspect the existence of a rather strong compound or of a regular arrangement of the bromide ions in the lead chloride crystal lattice. Such a factor would reduce the activities of both components and would tend to annul the effect of any factor which produces abnormally large activities. This striking result is entirely unpredictable from the freezing point diagram, which gives no indication of any abnormality.

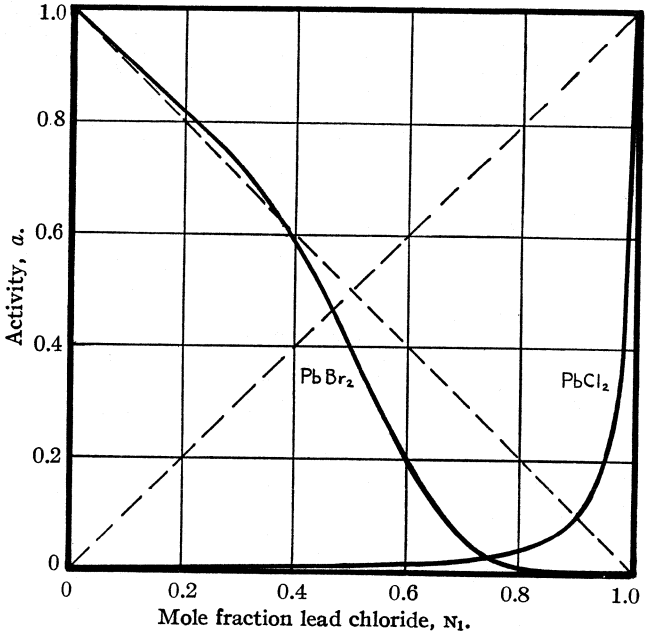


Fig. 3.—Activity curves for the system lead chloride–lead bromide at 200°.

Measurements of the partial vapor pressures of this system by Jellinek and Bolubowski,[4] who found Raoult's law obeyed by the vapor pressures at temperatures from 660 to 740°, indicate that at these high temperatures the compound is completely dissociated and that the constituents form ideal liquid solutions. Salstrom and Hildebrand,[5] making an electrochemical investigation of molten solutions of these fused salts at temperatures from 450 to 550° and at mole fractions 1 to 0.45 of lead bromide, found that the activities in this range are less than the simple mole fractions. Although, making allowance for the differences in temperature, the values they give at mole fractions 0.5 and 0.45 of lead bromide are in good agreement with those herein obtained, those given at higher concentrations of lead bromide are in marked disagreement.

[4] Jellinek and Bolubowski, *Z. physik. Chem.*, Abt. A, **147**, 461 (1930).

[5] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).

For the existence of any one arrangement of foreign ions in a crystal lattice to be more probable than any other of the infinite variety of possible arrangements, that distribution must give the most stable solution. Tammann[6] has strongly supported the assumption which originated with him that a regular or "normal" distribution is to be expected in solid solutions and that the most stable arrangements can be represented as multiples of one-eighth mole of one of the two constituents. . Thermodynamically, the greatest total free energy change of solution must occur at some composition which can be expressed as a multiple of one-eighth mole in order

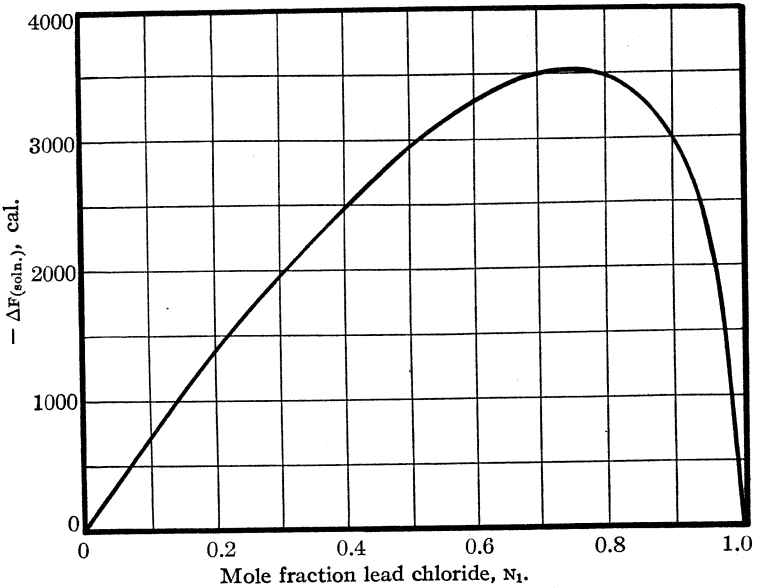


Fig. 4.—Variation with composition of the free energy change for the reaction $N_1\ PbCl_{2(s)} + N_2\ PbBr_{2(s)} = N_1\ PbCl_2 \cdot N_2\ PbBr_{2(s.soln.)}$ at 200°.

to be in accord with the above views. The total free energy of solution as employed here signifies the free energy change involved in the formation of one mole of solution from the pure constituents at a given temperature. It can be calculated from the partial molal free energies by the relationship $\Delta F_{(soln.)} = N_1\Delta\bar{F}_1 + N_2\Delta\bar{F}_2$. When this is done for the lead chloride–lead bromide system and the results are plotted against the mole fraction of lead chloride, as in Fig. 4, one observes a rather sharp maximum at six-eighths mole of lead chloride. Tammann's conclusions are based upon the striking discontinuities observed in variations of the intensity of chemical action with the concentration. These resistance limits occur at compositions which can be expressed as multiples of one-eighth mole of one of the two constituents. In accordance with these ideas one would predict

[6] Tammann, *Z. anorg. allgem. Chem.*, **107**, 1 (1919).

that the lead chloride–lead bromide solid solutions would exhibit a discontinuity in chemical action at mole fraction 0.75 of lead chloride.

Summary

1. The energy changes of solid lead chloride upon dilution with lead bromide have been determined at mole fractions of lead chloride varying from 1 to 0.200, between the temperatures of 200 and 300°.

2. The solid solution containing 0.75 mole of lead chloride is shown to be the most stable.

3. The thermodynamic properties of these solutions are considered compatible with the existence of a regular arrangement of bromide ions in the lead chloride lattice.

4. A discontinuity in chemical action of the solid solutions at mole fraction 0.75 of lead chloride is predicted.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, METALLURGY AND CERAMICS, UNIVERSITY OF ALABAMA]

A NEW USE OF THE VACUUM TUBE IN ELECTROMETRIC TITRATIONS. I. POLARIZATION OF PLATINUM ELECTRODES IN OXIDATION AND REDUCTION REACTIONS[1]

BY J. L. KASSNER, R. B. HUNZE AND J. N. CHATFIELD

RECEIVED FEBRUARY 2, 1932 PUBLISHED JUNE 6, 1932

Introduction

Since the advent of the radio it is generally known that electrons are drawn across the tube by means of a positive potential impressed on the plate. The plate current in the tube is controlled largely by means of a grid which is placed between the filament and the plate. If a positive potential is placed on the grid, electrons flow to the plate in greater number, and if a negative potential is placed on the grid fewer electrons will flow to the plate, lowering the plate current. Goode[2] utilized the fact that the grid will not pick up electrons when it is charged negatively with respect to the filament and connected the indicator electrode directly to the grid. This same principle has been employed by other investigators.[3] In all of the investigations reported, in which a single electron tube was employed, it has been necessary to plot $\Delta E/\Delta v$ or to plot galvanometer deflections in place of ΔE to obtain the equivalence point. Daniels, Mathews and

[1] Paper presented before the Buffalo meeting of the American Chemical Society.

[2] Goode, THIS JOURNAL, **44**, 26 (1922).

[3] Calhane and Cushing, *J. Ind Eng. Chem.*, **15**, 1118 (1923); Treadwell, *Helv. Chim. Acta*, **8**, 89 (1925); Williams and Whitenack, *J. Phys. Chem.*, **31**, 519 (1927).

Williams[4] state that the characteristics of a vacuum tube should always be determined before it is used for any purpose, and since the characteristics of a vacuum tube vary with the age of the tube as well as with new tubes of the same type, the application of vacuum tubes to electrometric titrations has not been widely adopted. This investigation was started to find, if possible, a method of utilizing the vacuum tube in electrometric titrations in such a way that the results of the titrations are less dependent upon the characteristics of the tube and to avoid the necessity of plotting curves to obtain the equivalence point. The following "hook-up" and data are presented as evidence of how well this has been accomplished. A diagram of the apparatus is shown in Fig. 1.

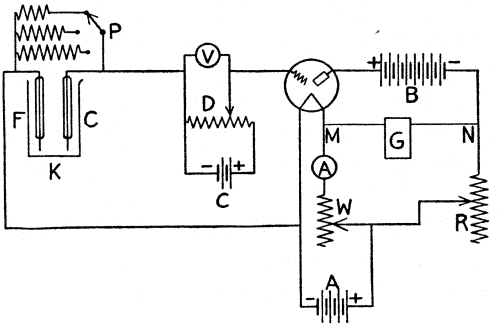


Fig. 1.—F and C, platinum electrodes, B. and S. No. 28 about 3 cm. long; P, shunt; V, voltmeter reading in units of 0.1 volt; D, potential divider; C, 4.5-volt C-battery; B, 22.5-volt B-battery; G, galvanometer of about 1000 ohm resistance; A in circle, milliammeter; W, 50-ohm variable resistance; R, 5000-ohm variable resistance; A, 6-volt storage battery. A motor-driven stirrer is not shown.

This apparatus differs from Goode's in that a positive potential is impressed on the grid of the vacuum tube; a Cunningham amplifier, 301A or R. C. A., 201 A, whose filaments operate normally at 6 volts, drawing 0.25 ampere; and the grid current has been employed to polarize bimetallic platinum electrodes which have been substituted for the monometallic system. Part of the grid current (the grid current is very small because of the construction of the vacuum tube) is shunted around the electrodes.

When electrodes have been placed in the solution to be titrated and the resistance R adjusted so that the galvanometer reads zero; the points M and N are at the same potential. Electrons are flowing through the tube in three distinct circuits: the filament, filament to grid, and filament to plate. The electrons that are picked up by the plate may be considered as flowing through the B-battery, R, and back to the A-battery. The strength of this current depends upon the temperature of the filament, the voltage of the B-battery, the value of R, and the potential impressed on the grid. The current in the three circuits will remain constant during the course of a titration as long as the potential difference between F and C remains constant if the other adjustments are not changed. A slight change in the potential between F and C will produce a corresponding

[4] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1929, p. 402.

change in the potential impressed on the grid. This will produce a relatively large change in the plate current, which will unbalance the system. M and N will no longer be at the same potential and the galvanometer will deflect.

Experimental

The theory of polarized electrodes has been studied in detail by Willard and Fenwick[5] and Van Name and Fenwick.[6] They have shown that polarized platinum electrodes owe their effect in electrometric titrations to gas reactions taking place on the surface of the electrodes and that the potential difference between the electrodes remains practically constant up to about 0.5 ml. of the equivalence point.

For the successful operation of this apparatus it is necessary for the potential difference between the electrodes to remain constant up to the equivalence point, and this has been accomplished by shunting part of the polarizing current around the electrodes. Shunted electrodes were first used by Foulk and Bawden.[7] They stated that no current flows through the solution when the drop in potential across the shunt is equal to the back e. m. f. due to polarization. For this reason it was thought that it would be necessary to control the shunt within narrow limits, but it was found that the shunt could be varied over a comparatively wide range without vitiating the results. The results of the titrations using different shunts are presented in Table I.

TABLE I

TITRATION OF APPROXIMATELY 0.1 *N* SODIUM THIOSULFATE WITH IODINE

V, 1.6 volts; filament current, 0.25 ampere; B-battery, 22.5 volts

Run	Iodine Calcd., ml.	Found, ml.	Error, ml.	Shunt P, ohms
1	25.15	25.13	0.02	20,000
2	25.15	25.12	.03	5,000
3	25.15	25.15	.00	35,000

No attempt was made to determine the absolute limits of the shunt. The calculated ml. are the average of three concordant determinations using starch as the indicator. When no shunt resistance was employed the needle of the galvanometer drifted off the scale after the addition of about 2 ml. However, it is possible to titrate with a shunt of infinite resistance if the correct voltage is impressed on the grid, but more difficulty is experienced in balancing the potentials. As is shown by the table, the end-point obtained by the electrometric method is slightly in advance of the end-point obtained by the starch indicator. Attention was also called to this fact by Foulk and Bawden.[8] It has been found that it is possible,

[5] Willard and Fenwick, THIS JOURNAL, **44**, 2504 (1922).

[6] Van Name and Fenwick, *ibid.*, **47**, 9, 19 (1925).

[7] Foulk and Bawden, *ibid.*, **48**, 2045 (1926).

[8] Foulk and Bawden, *ibid.*, **48**, 2047 (1926).

keeping the other conditions the same as those given in the table, to vary the shunt over the same range in the titrations of bichromate with ferrous ammonium sulfate, arsenite with bromate, and arsenite with iodine.

Reference to Fig. 1 shows that the potential impressed on the grid is less than the reading of the voltmeter, V, by the potential of the counter e. m. f. due to polarization. Since the plate current is a function of the potential impressed on the grid it can be seen why the system remains balanced up to the equivalence point if the potential difference between the electrodes remains constant, and then suddenly changes at the end-point. Table II is offered in support of the theory that the potential difference between the electrodes remains constant up to the equivalence point if the right conditions are employed. The slight fluctuations in the potential difference from 1 to 13.84 ml. are, undoubtedly, the result of experimental error.

TABLE II

POTENTIAL DIFFERENCE BETWEEN POLARIZED PLATINUM ELECTRODES IN THE TITRATION OF SODIUM ARSENITE WITH POTASSIUM BROMATE

Ml. of 0.1 N $KBrO_3$	E. m. f. with respect to N-calomel electrode: C, cathode, mv.	F, anode, mv.	F minus C, mv.	Galv., zero center
0.00	284	529	245	0
1.00	270	527	257	2, left
6.00	269	525	256	3, left
12.00	266	525	259	6, left
13.40	268	528	260	8, left
13.70	269	529	260	9, left
13.80	266	525	259	10, left
13.83	262	527	265	10, left
13.84	359	622	263	12, left
13.85	679	872	193	Extreme right

In making these measurements a 50,000-ohm resistance was kept in series with the electrodes, but even then enough current was drawn from them, in the process of balancing, to change the potential of the electrodes slightly. In carrying out titrations in which the potential of the electrodes was not measured, the drift of the galvanometer needle was of less magnitude. The two additions of potassium bromate from 13.83 ml. to 13.85 ml. were made with the aid of a stirring rod, and the readings are offered merely to show that the change at the equivalence point is very sharp. The change is confined to within 0.05 ml. of 0.01 N solution in a volume of 250 to 300 ml.

The main objection offered to the use of polarized bimetallic electrodes is that the approach of the end-point is indicated only about 0.3 ml. in advance. This indication is far enough in advance for the successful use of this apparatus, because the operator has only to control the buret and

observe the galvanometer, since it is not necessary to make any adjustments after the titration is begun. Furthermore, this "hook-up" possesses an additional characteristic in that the indication of the approach can be controlled by placing the electrodes in the solution in such a position that there will be a slight difference in the composition of the solution surrounding one of them as the equivalence point is approached. This difference in composition will be only momentary due to the process of mixing. This will be manifested by a temporary instability of the galvanometer. The galvanometer again becomes stable if the addition of the titrating solution is discontinued. After the indication of the approach[9] of the end-point is obtained, the titration can be continued dropwise until the needle of the galvanometer "kicks" off the scale and remains there.[10]

If the operator does not wish to rely upon the indication of the approach in order to avoid overstepping the end-point, a small portion of the unknown solution can be withheld in a small dropper until the apparent end-point is obtained. Upon the addition of this small portion the needle will return to its former position. The end-point can then be approached dropwise.

In order to show that it is not necessary to control the different variables in this apparatus within narrow limits the following data are presented.

The Bichromate–Ferrous Iron Reaction.—The results of titrations with the apparatus described in this paper in comparison with those obtained with the Wendt electrometric titration apparatus are given in Table III.

[9] Best results are obtained when the standard solution is added at a constant rate of about 1 ml. in seven seconds up to this point.

[10] For three of the determinations (arsenite with iodine, arsenite with bromate, and thiosulfate with iodine) reported in this paper the optimum positions of the electrodes were found to be as follows. With the stirrer placed in the center and near the bottom of a 400-ml. beaker containing 200–250 ml. of solution, electrode F with the wire running in an almost horizontal position toward the back of the beaker was placed about 2 cm. above the stirrer and to the extreme right of the beaker. Electrode C was placed to the left of the stirrer with the wire running almost in a horizontal position toward the front of the beaker a little below the stirrer, the stirrer rotating in the direction of electrode F. The solution was added from a buret placed about 1 cm. to the left and about 1 cm. in front of the stirrer. If the indication of the approach of the end-point is given too soon it can be postponed by lowering electrode F, or if too late it can be advanced by raising elecctrode F. After a little experience the operator will have no difficulty in adjusting the electrodes so as to obtain an indication of the approach at the point he most desires. Although not necessary to do so, it has been found advantageous to reverse the relative positions of electrodes F and C in the titration of potassium bichromate with ferrous ammonium sulfate, for when the solution is thrown upon electrode C in this titration, the indication of the approach is obtained by the needle "kicking" left, whereas, in the other three titrations, "kicks" to the left were obtained when the solution was thrown upon electrode F. By left is meant the opposite direction to that in which the needle of the galvanometer goes at the end-point.

TABLE III

TITRATION OF APPROXIMATELY 0.1 *N* BICHROMATE WITH FERROUS SULFATE

Run	Tube	$FeSO_4$ Calcd., ml.	$FeSO_4$ Found, ml.	Error, ml.	Current Plate, Ma	Current Filament, Ampere	B-battery, volts	*V* in volts	*P* in ohms
1	1	26.60	26.60	0.00	1.25	0.25	22.5	1.6	20,000
2	1	26.60	26.57	.03	0.65	.20	18.0	1.2	15,000
3	1	26.60	26.59	.01	2.50	.27	36.0	2.0	25,000
4	2	26.60	26.60	.00	2.10	.26	36.0	2.0	25,000
5	2	26.60	26.62	.02	0.51	.20	18.0	1.2	15,000

Initial volume, 200–250 ml.; deflection of galvanometer to extreme right.

In most cases the needle drifted five or more spaces to the left during the course of the titration. The calculated values are the average of several concordant determinations with the Wendt apparatus.

The following titrations were carried out and essentially the same results were obtained when the variables were varied as shown in Table III: sodium thiosulfate with iodine, sodium arsenite with iodine and with bromate. Other tubes of the same type but with different characteristics were used with equal success.

The conditions given in Run 1 of Table III have been selected as the optimum. No attempt was made to determine the exact limits of the different variables. Each variable can be varied independently over the following range if the other factors are left constant as given in Run 1: P, 5000–35,000 ohms; V, 0.4–2.2 volts; B, 18–45 volts; filament current, 0.18–0.27 ampere. These are not absolute limits.

Accuracy.—Approximately 0.01 *N* solutions were prepared by diluting the 0.1 *N* solutions employed above ten times and for this reason the calculated values of the 0.01 *N* have been considered numerically equal to those of the 0.1 *N*. Table IV gives the results of a typical titration.

TABLE IV

TITRATION OF APPROXIMATELY 0.1 *N* BICHROMATE WITH FERROUS SULFATE

	1	2	3
Ferrous sulfate, calcd. ml.	26.60	26.60	26.60
Ferrous sulfate, found ml.	26.64	26.62	26.65
Error, ml.	0.04	0.02	0.05

Total volume 200–250 ml.

When the galvanometer employed had a sensitivity of 0.5 microampere per millimeter, a deflection of only ten scale divisions was obtained with 0.01 *N* solutions but when a galvanometer which had a sensitivity of 0.025 microampere per millimeter was employed a deflection of more than thirty scale divisions per drop was obtained. The addition of one drop of 0.001 *N* iodine solution to a volume of 250 ml. of a slightly acid solution gave a deflection of twenty scale divisions with the latter galvanometer. Because of the extreme precautions that must be taken when working with 0.001 *N*

solutions it will be necessary to delay the report on this dilution until a later date.

Summary

1. A positive potential has been impressed upon the grid instead of the usual negative.

2. The polarization of platinum electrodes by means of a grid current has been used to advantage in the electrometric titrations of some oxidation–reduction reactions.

3. The different variables in this "hook-up" may be varied over a range of 20% without vitiating the results.

4. The equivalence point is indicated by the "kick" of a sensitive galvanometer and possesses the following characteristics: (a) approach is indicated, (b) high sensitivity, (c) over-stepping is immediately apparent, (d) the plotting and recording of readings is unnecessary, (e) tubes of the same type give the same equivalence point, (f) adjustments are unnecessary during titration.

UNIVERSITY, ALABAMA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN, CHLORPHENOL RED AND METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS[1]

BY ELWYN F. CHASE AND MARTIN KILPATRICK, JR.

RECEIVED FEBRUARY 2, 1932 PUBLISHED JUNE 6, 1932

A great part of the work in the colorimetric determination of hydrogen-ion concentration has been based on the incorrect assumption that equal color in solutions of equal indicator concentration meant equal hydrogen-ion concentration. That this assumption leads to errors of considerable magnitude has been clearly pointed out by Güntelberg and Schiödt.[2] They show that for the case studied by Szyszkowski[3] the error due to the above assumption amounted to several hundred per cent. Consequently, this error is of the greatest importance and a clear understanding of the factors involved is essential.

An indicator is nothing more than a weak acid, or base, where the acid form, or basic form, or both, is colored due to some structural rearrangement. Thus we can have a buffer system just as with any weak electrolyte

[1] Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

[3] Szyszkowski, *ibid.*, **58**, 420 (1907).

and the classical dissociation constant is a good measure of the acid strength. If we consider the acid HI the classical dissociation constant is

$$K_c = \frac{C_{H^+} \cdot C_{I^-}}{C_{HI}} \quad (1)$$

where C_{H^+} really represents $C_{H_3O^+}$. At the half transformation point $C_{HI} = C_{I^-}$ and

$$K_c = C_{H^+} \quad (2)$$

Now it is generally known that K_c changes with change in electrolyte concentration. In the case of monobasic acids these changes depend not only on the electrolyte concentration but also on the particular acid and electrolyte.[4] The magnitude of these changes will also depend on the ion charge types involved but this will not affect the general equations derived below. If we consider two solutions I and II at the half change point or any other degree of transformation, *i. e.*, C_{I^-}/C_{HI} ratio, from equation (2) it follows that

$$\left(\frac{C_{H^+}}{K_c}\right)_I = \left(\frac{C_{H^+}}{K_c}\right)_{II} \quad (3)$$

If I is the known and II is the unknown, then

$$(C_{H^+})_{II} = (C_{H^+})_I \cdot \frac{(K_c)_{II}}{(K_c)_I} \quad (4)$$

an equal color means equal hydrogen-ion concentration when $(K_c)_{II}/(K_c)_I$ is equal to unity. In other words, $(K_c)_{II}/(K_c)_I$ is the term expressing the so-called "salt error" of indicators. The ratio $(K_c)_{II}/(K_c)_I$ may change several fold[4] so that the determination of the classical dissociation constants of indicators is essential to the use of the colorimetric method. The present paper deals with the determination of the classical dissociation constants of bromcresol green, chlorphenol red and methyl red in aqueous potassium chloride solutions.

The method of determining the classical dissociation constant depends upon having solutions of suitable known hydrogen-ion concentration and determining experimentally the ratio of the basic and acid forms of the indicator in such solutions. Substitution of these values in equation (1) gives the dissociation constant directly. This method has been used by Friedenthal[5] and improved upon by Gillespie.[6] For indicators having half-change points around 0.01 molar hydrogen-ion concentration, it is convenient to use solutions of strong acid as standard but it is not practicable to work in glass with large amounts of salt present at concentrations of strong acid much below 1×10^{-3}. Besides, in unbuffered solutions of this sort one must take into account the buffering action of the

[4] For examples see Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931).

[5] Friedenthal, *Z. Elektrochem.*, **10**, 114 (1904); Salm, *Z. physik. Chem.*, **57**, 471 (1906).

[6] Gillespie, THIS JOURNAL, **42**, 742 (1920).

indicator system.[7] In the present study the standards have been the buffer systems of benzoic acid–benzoate, acetic acid–acetate, cacodylic acid–cacodylate and hexahydrobenzoic acid–hexahydrobenzoate. In the first case the hydrogen-ion concentrations were those calculated from the values of the classical dissociation constant of benzoic acid in potassium chloride solutions as given by Chase and Kilpatrick.[4] In the other cases the hydrogen-ion concentrations were determined by means of the quinhydrone electrode under the same assumptions used in the standardization of the benzoic acid–benzoate system.[8]

Experimental Method

As preliminary experiments showed that different samples of indicator gave different values, we attempted to obtain the purest possible samples of the indicators.[9] Two samples of bromcresol green (tetrabromo-*m*-cresolsulfonephthalein) were used. The first was crystallized from acetic acid. The second was also crystallized from glacial acetic acid and analysis showed 44% bromine as against a calculated value of 45.8%. The indicator solutions were prepared by shaking a weighed amount of the indicator acid with a dilute solution of sodium hydroxide containing the calculated amount to form the sodium salt. The solution was then centrifuged and diluted to a convenient concentration. Preliminary experiments[10] with another indicator (bromphenol blue) have shown that in the presence of sodium hydroxide of concentration 3×10^{-3} molar and an indicator concentration of 2×10^{-5} molar the blue color disappears completely in about fourteen days. This change seems to be proportional to the hydroxyl-ion concentration and from a study of the increase in the rate of the reaction with increasing potassium chloride concentration (primary kinetic salt effect) appears to be a reaction between two ions. Since the solutions gave tests for the bromide ion, it seems likely that the bromine is replaced by the hydroxyl ion in the compound. For this reason we avoided using the method recommended by Clark[11] in which the indicators are ground up with 0.01 molar sodium hydroxide solutions. In fact in later work we have been using the following method to carry out the neutralization more quickly and thus avoid an excess of sodium hydroxide. The indicator is dissolved in alcohol, the calculated amount

[7] This has been pointed out by Fawcett and Acree, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930), and Kolthoff, THIS JOURNAL, **53**, 825 (1931).

[8] Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

[9] The bromcresol green and chlorphenol red were specially purified and furnished to us through the kindness of Drs. D. Twiss and W. C. Harden of the Chemical Research Laboratory of Hynson, Westcott and Dunning Co., Baltimore, Md.

[10] Experiments carried out with C. E. Gulezian.

[11] Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, Md.

of aqueous sodium hydroxide added, the alcohol evaporated under reduced pressure and the residue taken up in distilled water.

Two samples of chlorphenol red (dichlorophenolsulfonephthalein) were used. The first was purified by repeated solution in sodium carbonate and precipitation by hydrochloric acid. This sample did not dissolve completely in sodium hydroxide. A second sample purified by Harden[12] dissolved completely and immediately in very dilute sodium hydroxide. The second sample gave the following analysis: calcd., sulfur, 7.58; chlorine, 16.76. Found: S, 7.60; Cl, 16.66. A comparison of the dissociation constants of these samples will be given later.

Methyl red (*o*-carboxybenzene-azo-dimethylaniline) was purified by repeated crystallization from toluene. The sample gave a sharp melting point between 176 and 177°.

The stock solutions of the indicators were diluted to a concentration of 5×10^{-4} molar and contained potassium chloride ranging from 0.1 to 3 molar. The colorimeter was of the Gillespie type and is described by Clark.[13] In all cases the acid form and the basic form were obtained by adding the calculated amount of hydrochloric acid or sodium hydroxide for over 99% conversion.

TABLE I

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: benzoic acid–benzoate, acetic acid–acetate, hexahydrobenzoic acid–hexahydrobenzoate. Temp., about 25°; indicator, about 5×10^{-5} mole per liter

Electrolyte KCl + NaX moles per liter	Average $K_c \times 10^5$	Number of detns.	a. d., %
0.1000	3.07 (2.33*k*)	6	3.5
0.5000	4.03 (3.13*k*)	5	2.6
1.000	3.61	9	6.4
1.500	3.46	6	3.6
2.000	2.93	5	5.8
2.500	2.55	6	4.9
3.000	2.38	3	3.8

X, anion of acid used in buffer. *k*, values chosen by Kolthoff.

Table I gives the results with bromcresol green. Column I gives the electrolyte concentration, which is largely potassium chloride. Column II gives the average value of K_c with a value calculated from the values of Kolthoff, given in his recent survey of indicator constants.[14] Kolthoff gives the values in terms of pK_1 and states that the accuracy is supposed to be within 0.05 of a logarithmic unit (12% in K_1). K_1 does not represent the classical dissociation constant but a dissociation constant defined by the equation

[12] Harden, THIS JOURNAL, **52**, 4611 (1930).

[13] Clark, Ref. 11, p. 169.

[14] Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

$$pK_1 = P_H - \log \frac{C_B}{C_A} \quad (5)$$

where P_H is the Sörensen P_H. The classical dissociation constant is related to this constant (K_1) by the equation

$$pK_c = pK_1 - pf_H + 0.04 \quad (6)$$

$-\log f_H$ was evaluated, with sufficient accuracy, from the empirical equations of Bjerrum and Unmack[15] and K_c was calculated from the values of Kolthoff for K_1. Our observed values, which are higher than those given by Kolthoff, were obtained with two different indicator samples and three different buffer systems.

TABLE II

THE CLASSICAL DISSOCIATION CONSTANT OF CHLORPHENOL RED IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: Cacodylic acid–cacodylate. Temp., about 22°. Indicator, about 2.5×10^{-5} moles per liter

Electrolyte, KCl + NaX, moles per liter	Average $K_c \times 10^7$	Number of detns.	a. d., %
0.1000	11.0 (10.7*k*)	3	6.7
0.5000	13.4 (13.5*k*)	3	5.4
1.000	16.2	2	1.9
1.500	13.1	2	2.1
2.000	13.2	2	2.3
2.500	9.45	2	4.9
3.000	7.90	2	10.0

X, cacodylate. *k*, values chosen by Kolthoff at 20°.

Table II gives the results for chlorphenol red in cacodylic acid–cacodylate buffers in potassium chloride solutions. The results with the first sample

TABLE III

THE CLASSICAL DISSOCIATION CONSTANT OF METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: Acetic acid–acetate. Temp., about 22°. Indicator, about 1.3×10^{-5} moles per liter

Electrolyte, KCl + NaX, moles per liter	Average $K_c \times 10^6$	Number of detns.	a. d., %
0.1000	10.4 (10.7*k*)	5	2.2
0.5000	9.21 (10.7*k*)	3	2.9
1.000	7.75	2	5.8
1.500	6.25	2	7.8
2.000	5.33	2	2.6
2.500	3.61	3	3.8
3.000	2.90	2	12.0

X, acetate. *k*, value chosen by Kolthoff at 20° for electrolyte concentrations from zero to 0.5 mole per liter ($10.7 \times 10^{-6} \pm 12\%$).

[15] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **9**, 1 (1929)

of indicator were much lower and are not included. For example, the dissociation constant for the first sample at one molar potassium chloride concentration was 7.7×10^{-7} as compared with 16.2×10^{-7} for the second sample.

Table III gives the results for methyl red. Methyl red is of particular interest in that it is an indicator of the ampho-ion type. Considering the structure

$$(CH_3)_2N—C_6H_4—N_2—C_6H_4—COOH$$

the molecule contains a basic group as well as an acid group. The amino group will tend to pick up protons to form the ampho-ion

$$(CH_3)_2NH^+—C_6H_4—N_2—C_6H_4—COO^-$$

In acid solution we have the form

$$(CH_3)_2NH^+—C_6H_4—N_2—C_6H_4—COOH$$

and in basic solution

$$(CH_3)_2N—C_6H_4—N_2—C_6H_4—COO^-$$

The dissociation constant is related to the dissociation constant at zero ion concentration by the equation

$$K_c = K_{c_0} \frac{f_{HI^\pm}}{f_{H^+} f_{I^-}}$$

Now Bjerrum[16] has shown that in dilute solution an ampho-ion behaves like a neutral molecule and in more concentrated solution like two ions. Consequently in very dilute solution

$$K_c = K_{c_0} \frac{1}{f_1^2}$$

Thus in dilute solution an exponential salt effect would be expected. In more concentrated solution the activity factor would be such

$$K_c = K_{c_0} \frac{f_1^2}{f_1^2}$$

that a linear salt effect would be expected. The curve for methyl red in Figure 1 shows this effect. The exponential effect below 0.1 molar was not investigated due to the fact that the assumptions involved in the electrometric method for determining the hydrogen-ion concentration are not valid below 0.1 molar. Güntelberg and Schiödt[2] do indicate the exponential part in the case of methyl orange. In this connection we cannot agree with the statement of Kolthoff[14] that the salt error of methyl orange is extremely small between 0.0 and 0.5μ. If we express the salt error as K_c/K_{c_0} and use the results of Güntelberg and Schiödt, the error is 32% between $\mu = 0.0$ and $\mu = 0.1$.

The curves for bromcresol green and chlorphenol red show that K_c increases with increasing electrolyte concentration, passes through a maximum and then decreases.

[16] Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

The Colorimetric Method.—In using the colorimetric method to determine the hydrogen-ion concentration of an unknown solution, one may simply reverse the method employed here in determining the dissociation constant of the indicator, that is, the ratio of the acid form to the basic form of the indicator is determined and the concentration of the hydrogen ion calculated from the equation

$$C_{H^+} = K_c \frac{C_A}{C_B}$$

where K_c is the correct value of the dissociation constant of the indicator for the particular electrolyte, electrolyte concentration and medium used.

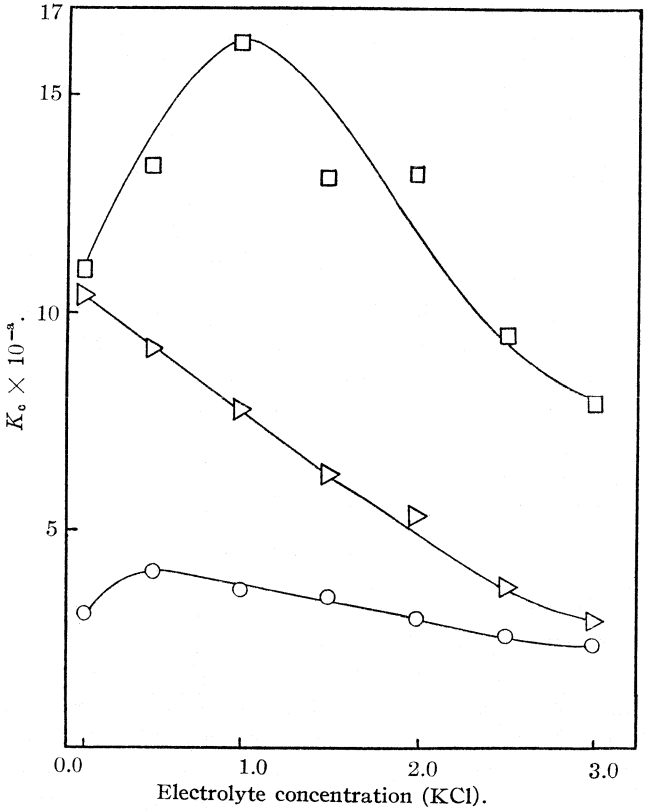


Fig. 1.—K_c for bromcresol green, chlorphenol red and methyl red in potassium chloride solutions: ○, B.C.G. (scale × 10^{-5}); □, C.P.R.(scale × 10^{-7}); ▷, M.R. (scale × 10^{-6}).

More often the unknown is matched with a standard and the hydrogen-ion concentration calculated by equation (4). In other words the ratio of the values of the dissociation constant of the indicator in the unknown and in the standard must be known. At present these standards are

usually given in Sörensen pH or $p\alpha H$ units, because the electrometric method is considered the standard. The resulting confusion can be avoided in dealing with aqueous solutions by calibrating a suitable set of standard solutions in terms of the hydrogen-ion concentration. A convenient standard is a buffer system: 0.01 molar in a suitable monobasic acid, 0.01 molar in the salt of the same acid and 0.09 molar in potassium chloride. The hydrogen-ion concentration of such buffers can be determined electrometrically, catalytically or colorimetrically, the measurements being referred directly to a solution of strong acid. In order to standardize colorimetrically one would determine the dissociation constants of a less sensitive indicator and then use that indicator to standardize a buffer system of an acid of slightly lower dissociation constant than the indicator. By extending this process to weaker acids the range could be extended.

Table IV gives the values of $K_c/K_{c(0.1)}$ for the three indicators and Fig. 2 presents these ratios graphically. Figure 2 also includes the $K_c/K_{c(0.1)}$ values for the acids used in determining the dissociation constant of the indicators.

TABLE IV

THE $K_c/K_{c(0.1)}$ RATIOS IN POTASSIUM CHLORIDE SOLUTIONS

Electrolyte, KCl + NaX, moles per liter	B. C. G.	C. P. R.	M. R.
0.1	1.00	1.00	1.00
0.5	1.31	1.22	0.89
1.0	1.18	1.48	.75
1.5	1.13	1.20	.61
2.0	0.95	1.20	.51
2.5	.83	0.86	.35
3.0	.78	.72	.28

In order to determine the hydrogen-ion concentration the unknown is matched with the standard at equal indicator concentration and the hydrogen-ion concentration of the standard multiplied by the appropriate value from Table IV. If another concentration of electrolyte is used as standard then we simply multiply the above values by the $K_{c(0.1)}/K_{c(\text{standard})}$ ratio. If another electrolyte than potassium chloride is present in the unknown it would be necessary to know the dissociation constant of the indicator in a solution of that electrolyte at the concentration in question. The magnitude of these differences can be seen from a comparison of the dissociation constants of acetic acid in potassium chloride and sodium chloride solutions as taken from Larsson and Adell.[17] The differences up to 0.2 molar are within the experimental error and then increase so that at 3 molar the difference is 12%. Harned and Murphy[18]

[17] Larsson and Adell, *Z. physik. Chem.*, [A] **156**, 352 (1931).

[18] Harned and Murphy, THIS JOURNAL, **52**, 5079 (1930).

report differences at 0.1 molar concentration. For bromphenol blue Güntelberg and Schiödt give K_c in 3 molar potassium chloride as 11.0×10^{-5} and in 3 molar sodium chloride as 9.4×10^{-5}. For higher valence types the differences would be greater and for accurate work it would be necessary to know the dissociation constant in the medium used. It might be emphasized here that no method of expressing the salt error will avoid these second order effects. The same statement should be made in regard to the effect of non-electrolytes and this part of the solute effect may be more important than is generally realized. In any case it is believed that the above method of expressing salt error in indicator work calls attention to the magnitude of the effect and gives a simple method of correcting for it.

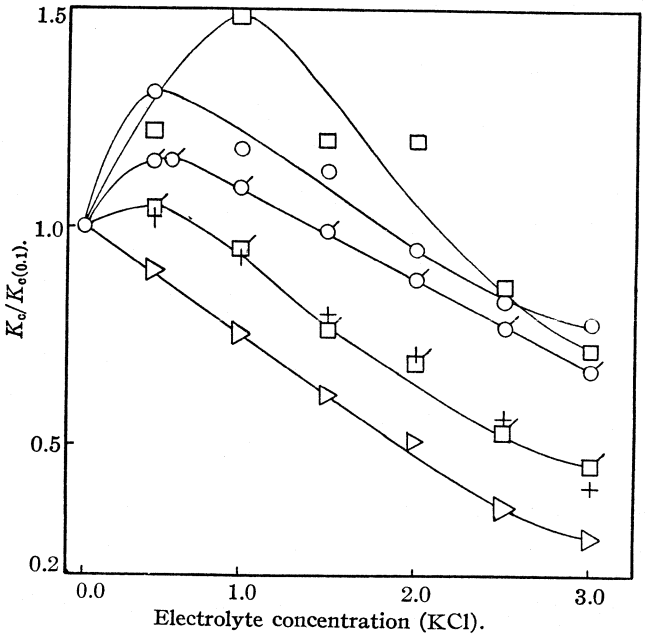


Fig. 2.—$K_c/K_{c(0.1)}$ for B. C. G., C. P. R., M. R., benzoic acid, acetic acid and cacodylic acid in potassium chloride solutions: ○, B. C. G.; □, C. P. R.; ▷, M. R.; ○-, benzoic acid; □-, cacodylic acid; +, acetic acid.

Summary

The classical dissociation constants of bromcresol green, chlorphenol red and methyl red in potassium chloride solutions have been determined.

A simple method of expressing salt errors in colorimetric determinations of hydrogen-ion concentration has been given.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ABSORPTION OF OXYGEN BY BENZALDEHYDE

BY H. J. ALMQUIST AND G. E. K. BRANCH

RECEIVED FEBRUARY 9, 1932 PUBLISHED JUNE 6, 1932

Introduction

The reaction of oxygen with benzaldehyde has been the subject of much investigation since the time of Wöhler and Liebig,[1] who observed that benzaldehyde is converted into benzoic acid in air, more rapidly in the light. Excellent historical reviews of the general subject of autoxidations have been prepared by Moureu and Dufraisse[2] and by Jorissen and Belinfante.[3] Bibliographies more particularly concerned with this reaction may be found in recent papers by Jorissen and van der Beek,[4] Bäckström and Beatty,[5] and Raymond.[6] Since these lists are practically complete it is unnecessary to repeat all of the references here.

The reaction has aroused much interest because it has been found that traces of other substances may either accelerate or inhibit the absorption. The influence of an inhibitor disappears after a period of time during which the inhibitor is itself oxidized, even though it may be a substance that in the pure state would not be affected appreciably by oxygen.

Apart from the influence of inhibitors and accelerators many peculiarities have been found in the reaction. These may be summarized as follows. (1) The reaction is photosensitive. (2) The reaction is probably a chain reaction both in the dark and in the light. (3) Earlier rate measurements have usually shown an induction period. (4) The rate constantly diminishes as time proceeds. (5) The walls of the containing vessel seem to play a part in the reaction, although there is little agreement on this point among investigators. (6) The reaction is presumably an excellent example of consecutive reactions, the first step being the formation of an intermediate peroxide, the second step the interaction of the peroxide with benzaldehyde to form benzoic acid.

We have investigated to some extent the influence of change of oxygen pressure on the rate of the reaction, but our chief efforts have been directed toward determining the distribution of absorbed oxygen between peroxides and benzoic acid during the reaction at a constant pressure of oxygen. In the present paper we shall report on the results obtained when, as far as possible, only benzaldehyde, oxygen and the products of their interaction are present.

[1] Wöhler and Liebig, *Ann.*, **3**, 253 (1832).

[2] Moureu and Dufraisse, *Chem. Rev.*, **3**, 113 (1927).

[3] Jorissen and Belinfante, *Rec. trav. chim.*, **48**, 711 (1929).

[4] Jorissen and van der Beek, *ibid.*, **49**, 138 (1930).

[5] Bäckström and Beatty, *J. Phys. Chem.*, [9] **35**, 2530 (1931).

[6] Raymond, *J. chim. phys.*, **28**, 480 (1931).

Materials

Benzaldehyde.—The benzaldehyde was purified by many fractional distillations in a current of dry carbon dioxide gas. The apparatus was so arranged that as many fractionations as desired could be obtained without contact between the benzaldehyde and air, stopcocks or rubber. The purification was continued until the usual induction period in the reaction of benzaldehyde with oxygen had disappeared. The product was stored in the dark under an excess pressure of carbon dioxide, in a flask so constructed as to permit a stream of gas to pass through and prevent the entrance of air when opened for the removal of samples.

Benzoic Acid.—Benzoic acid of a high grade was repeatedly recrystallized from water and dried over calcium chloride.

Oxygen.—The oxygen was obtained from a commercial manufacturer. Analysis showed it to contain more than 99.5% oxygen.

Variation of the Rate with the Oxygen Pressure.—When pure benzaldehyde is shaken at a constant speed in the dark and in contact with a fixed volume of oxygen, the rate of change of the logarithm of the oxygen pressure decreases with time much faster than would be expected from the using up of the benzaldehyde to form benzoic acid. Milas[7] has explained similar results in other autoxidations by assuming the removal of the active substance by an induced polymerization. This explanation is not valid in the case of benzaldehyde. On analyzing for the benzaldehyde left after the reaction had decreased considerably in rate, we found it to be practically equal to the original quantity less the benzaldehyde converted to benzoic acid and peroxides.

When similar experiments were performed with benzaldehyde containing 3% of benzoic acid the rate of change of the logarithm of the oxygen pressure was, after the first few minutes, slightly more constant than would be expected from the decrease in the concentration of the benzaldehyde. The reaction between benzaldehyde and oxygen is, therefore, of the first order with respect to oxygen. The rate is decreased probably by the action of small quantities of substances produced in the reaction. In the presence of benzoic acid the formation of these inhibitors is prevented or they rapidly reach a steady state concentration.

Table I shows the data from an experiment on the autoxidation of a benzaldehyde–benzoic acid mixture, the rate of reaction being measured by the decrease of the oxygen pressure with time. The total oxygen absorbed corresponded to 55 cc. at 25° and 760 mm. of mercury. The initial benzaldehyde and benzoic acid were equivalent to 263 cc. and 9.1 cc. of oxygen, respectively. The rate constant was calculated as $K = \mathrm{d} \log_{10} P/\mathrm{d}t$, where P is the oxygen pressure in mm. of mercury and t is the time in minutes.

[7] Milas, THIS JOURNAL, **52**, 734 (1930).

TABLE I

DATA ON THE REACTION OF A BENZALDEHYDE–BENZOIC ACID MIXTURE WITH A CONSTANT VOLUME OF OXYGEN

Time in minutes	Pressure of oxygen in mm.	$K \times 10^3$	Time in minutes	Pressure of oxygen in mm.	$K \times 10^3$
0	753.0		50	530.5	6.74
11	693.5	7.48	60	495.0	6.93
20	651.5	6.95	70	463.0	6.67
30	608.0	6.90	80	433.0	6.69
40	567.5	6.88			

The Distribution of Absorbed Oxygen.—The absorption of oxygen gas and the quantities of benzoic acid and of peroxides formed were measured during the reaction at 25° and 1 atmosphere pressure of oxygen and in the absence of light. The more important parts of the apparatus used are shown in Fig. 1.

The automatic gas buret, C, was filled with oxygen just before starting an experiment and then closed off from the remainder of the apparatus until needed. The buret was kept at a temperature of 25° by a water jacket and a water circulating system.

The reaction vessel, B, was immersed in a thermostat filled with water blackened by the addition of India ink. Before each experiment the vessel was thoroughly cleaned and steamed out. It was charged with a 2.25-cc. portion of benzaldehyde or a benzaldehyde–benzoic acid mixture under an atmosphere of carbon dioxide. The container above the reaction vessel was filled with a solution of potassium iodide in methyl alcohol and water. This solution was readily miscible with the autoxidized benzaldehyde.

The manometer, D, connected to the gas buret, C, was so adjusted that a very slight fall in pressure caused an electrical circuit to be broken. By the use of electric switches, etc., the breaking of the circuit was caused to activate a mechanism for lifting the mercury bottle, E. When the pressure in the system was restored to 1 atmosphere the circuit in D again closed and the ascent of E automatically stopped. The mechanism for raising E was composed of an electric motor, a speed-reducing gear and a small rotating shaft upon which a cord attached to E was wound. The manometer controlled the pressure with a variation of about 0.2% during the course of a reaction.

Reactions were started by filling the reaction vessel with oxygen after evacuating other gases, connecting in the gas buret and then shaking the vessel by the use of a mechanism driven by a constant speed motor. The time elapsed from the admission of oxygen until the shaker was started was three to five seconds. The volume of oxygen absorbed was noted at short intervals.

At a chosen time the potassium iodide solution was run into the reaction vessel and the shaker stopped. The iodine liberated by the action of the peroxides was titrated with sodium thiosulfate solution and, following this, the benzoic acid was titrated with sodium hydroxide solution. It was assumed that the following reaction took place on adding the potassium iodide solution to the contents of the reaction vessel.

$$C_7H_6O_3 + 3I^- + H^+ \longrightarrow C_7H_5O_2^- + I_3^- + H_2O$$

Each equivalent of iodine represents half a mole of peroxide and the loss of half a mole of acid. This benzoic acid was added to that found later by the titration with standard alkali. On this basis the absorbed oxygen in the form of peroxides and benzoic acid at the instant of the stopping of the reaction was calculated. That these assumptions give essentially the correct results is shown by the facts that the initial rate of formation of peroxides is equal to the rate of absorption, while the initial rate of formation of benzoic acid is practically zero, and that the sum of the peroxide and benzoic acid oxygen is

approximately equal to the oxygen absorbed. When necessary in the early stages of the reaction, known quantities of benzoic acid were added to the potassium iodide solution to furnish the required acid for the above reaction.

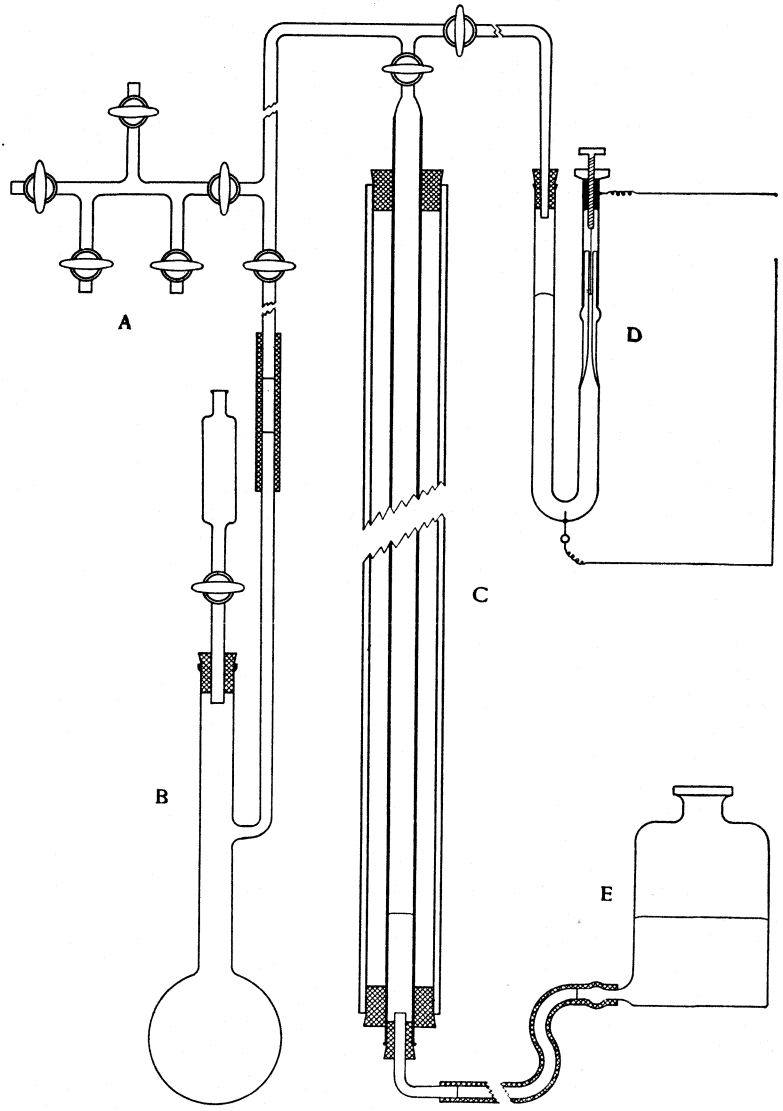


Fig. 1.—Automatic gas buret used for measuring the oxygen absorbed at constant pressure: A, connections to oxygen supply, manometer, vacuum pump and vent; B, reaction vessel and container for potassium iodide solution; C, buret tube with constant-temperature water jacket; D, mercury manometer which controls the mechanism for raising the mercury bottle; E, mercury bottle.

The sum of the peroxide and benzoic acid oxygen averaged about 3% less than the oxygen measured volumetrically. This discrepancy is probably real and due to the formation of substances not included in our analysis. Some indication of an unknown side reaction is found in the fact that benzaldehyde which has undergone extensive autoxidation acquires a yellow color and may produce small amounts of a yellow solid.[8]

In an effort to secure an explanation of this oxygen discrepancy we searched for the following substances: benzil, phenolic materials, carbon dioxide, carbon monoxide, peroxides that react rapidly with iodide ion only in strongly acid solution and peroxides that lose oxygen gas in the presence of iodide ion. All of these were found to be absent and would have been detected readily if present in quantities sufficient to explain the disagreement in our measurements.

In our method the complete time curve for the absorption of oxygen could be obtained by a single experiment, while the amounts of peroxides and benzoic acid could only be obtained for a particular instance by one experiment. It was necessary to perform many experiments over varying intervals of time in order to secure the data for the construction of the peroxide and benzoic acid time curves. The absorption time curve shown in Fig. 2 was taken from one of the faster reactions which was chosen as a standard. The unshaded points along this curve are those of the standard reaction, while the shaded points indicate the final total absorptions of the separate reactions. In some cases the results were weighted according to the agreement of the reaction with the standard. The results of the experiments started with the purified benzaldehyde are shown in Table II. The curves for the total absorption, the formation of benzoic acid, the formation of peroxides and the difference between the calculated and the

TABLE II

DATA ON THE REACTION OF THE PURIFIED BENZALDEHYDE WITH OXYGEN

Time of reaction, min.	Total absorption, cc.	Oxygen as peroxide, cc.	Oxygen as benzoic acid, cc.	Total oxygen by analysis, cc.	Oxygen discrepancy, cc.
6.02	9.35	8.05	1.17	9.22	0.13
8.00	11.30	9.05	2.45	11.50	— .20
12.50	17.22	13.75	3.26	17.01	.21
16.32	20.88	15.13	5.50	20.63	.25
19.78	26.00	16.65	8.85	25.50	.50
24.00	27.40	15.38	11.12	26.50	.90
28.00	32.80	13.34	18.82	32.16	.64
30.12	36.65	12.09	23.98	36.07	.58
35.18	38.50	10.25	27.00	37.25	1.25
36.40	42.32	9.23	32.12	41.35	0.97
40.20	43.20	7.95	34.25	42.20	1.00
41.39	45.80	7.63	36.20	43.83	2.03
43.50	48.60	6.76	39.95	46.71	1.89
47.00	48.62	6.20	40.50	46.70	1.92
60.58	65.43	5.51	58.02	63.53	1.90
61.78	63.00	5.45	55.48	60.93	2.07

[8] A similar substance has been noted by Bäckström and Beatty in the autoxidation of mixtures of benzaldehyde and anthracene.

observed oxygen are shown in Fig. 2. All results are expressed in terms of volumes of oxygen at 25° and 760 mm. of mercury.

It is apparent from Fig. 2 that the benzoic acid is formed in a follow reaction between the peroxide and the benzaldehyde. The results also

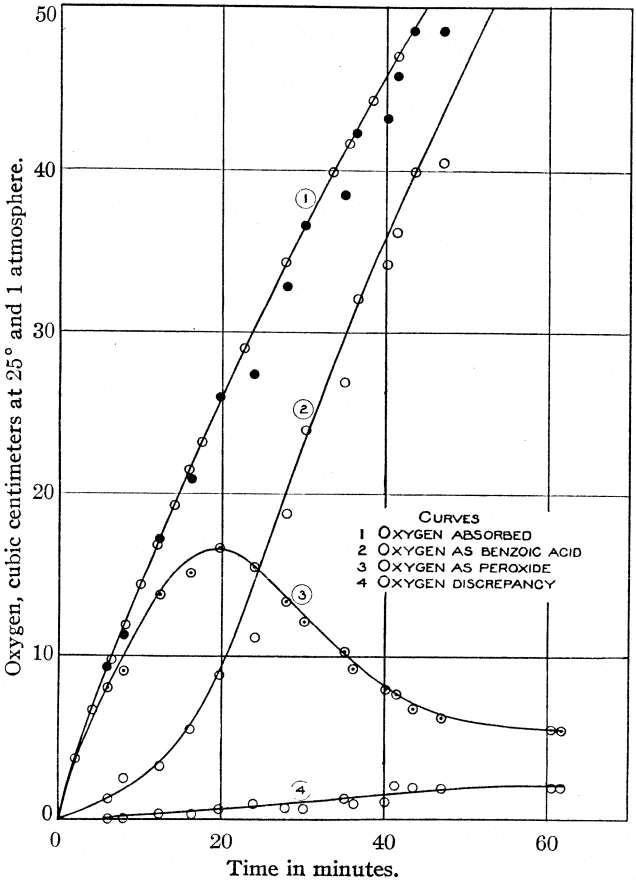


Fig. 2.—Reaction of purified benzaldehyde: curves showing the variation with time of, 1, the total oxygen absorbed, 2, the oxygen used to form benzoic acid, 3, the oxygen in the form of peroxides and, 4, the discrepancy between the volume of oxygen absorbed and the oxygen accounted for by analysis.

show that the rate of this reaction increases markedly as the reaction proceeds. Thus the rate of formation of benzoic acid is 0.3 cc. of oxygen per minute when 9.0 cc. of peroxide oxygen is first present, but it is 1.2 cc. per minute when the peroxide is again present in this amount in a later stage of the reaction. The increase in the rate is apparently due to the presence of benzoic acid. This relation was tested further by adding

benzoic acid equivalent to 9.1 cc. of oxygen in the usual charge of benzaldehyde. The data from these experiments are presented in Table III and Fig. 3 in the same manner as before.

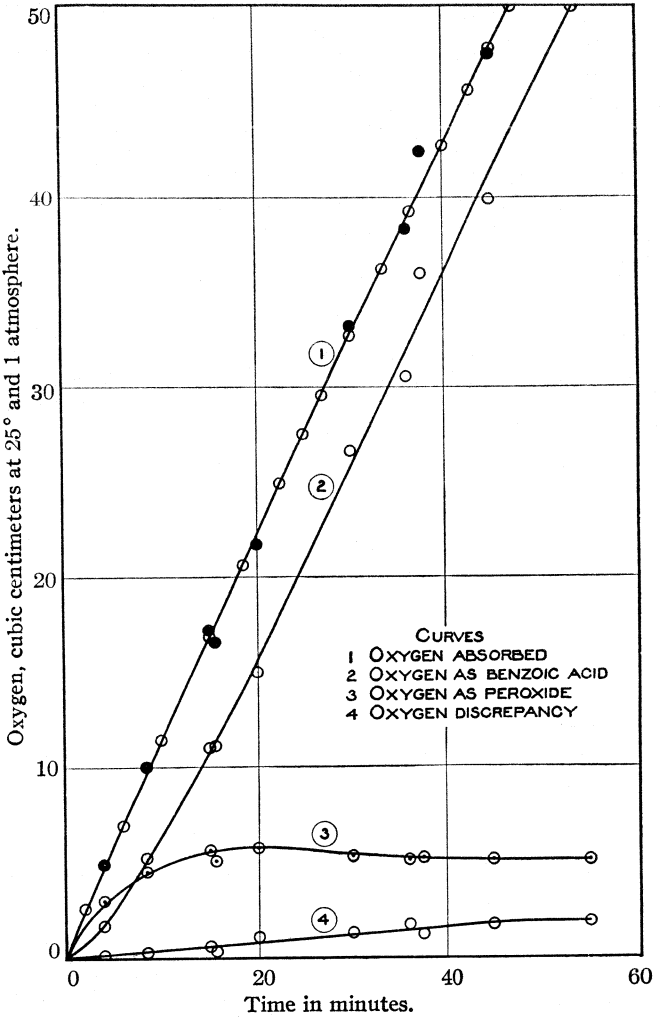


Fig. 3.—Reactions of the benzaldehyde–benzoic acid mixture: curves showing the variation with time of, 1, the total oxygen absorbed, 2, the oxygen used to form benzoic acid, 3, the oxygen in the form of peroxides and 4, the discrepancy between the volume of oxygen absorbed and the oxygen accounted for by analysis.

The rates of formation of benzoic acid at various concentrations of peroxide and benzoic acid are shown in Tables IV and V. A comparison of

TABLE III

DATA ON THE REACTION OF THE BENZALDEHYDE–BENZOIC ACID MIXTURE WITH OXYGEN

Time of reaction, min.	Total absorption, cc.	Oxygen as peroxide, cc.	Oxygen as benzoic acid, cc.	Total oxygen by analysis, cc.	Oxygen discrepancy, cc.
4.00	4.90	3.01	1.72	4.73	0.17
8.42	10.00	4.45	5.25	9.70	.30
15.00	17.20	5.64	11.00	16.64	.56
15.52	16.55	5.08	11.10	16.18	.37
20.00	21.80	5.73	14.95	20.68	1.12
30.00	33.20	5.31	26.60	31.91	1.20
36.00	38.35	5.10	31.55	36.65	1.70
37.60	42.40	5.20	36.01	41.21	1.19
45.02	47.73	5.09	40.92	46.01	1.72
55.10	58.35	5.11	51.40	56.51	1.84

TABLE IV

FORMATION OF BENZOIC ACID IN EXPERIMENTS STARTED WITH BENZALDEHYDE ONLY

Oxygen in the form of peroxides	Oxygen in the form of benzoic acid	Rate of formation of benzoic acid in cc. of oxygen per minute	Rate of formation of benzoic acid divided by the total peroxide concentration
9.0	1.5	0.30	0.33
11.0	2.1	.35	.32
15.6	4.8	.65	.42
16.6	8.0	1.00	.60
16.2	11.5	1.35	.83
15.0	15.6	1.50	1.00
13.6	20.1	1.55	1.14
12.5	23.0	1.55	1.24
10.6	28.8	1.40	1.32
8.9	33.9	1.25	1.40
7.4	38.5	1.10	1.49
6.6	42.6	1.05	1.59
5.9	49.1	1.00	1.69

TABLE V

FORMATION OF BENZOIC ACID IN EXPERIMENTS STARTED WITH THE BENZALDEHYDE–BENZOIC ACID MIXTURE

Oxygen in the form of peroxides	Oxygen in the form of benzoic acid	Rate of formation of benzoic acid in cc. of oxygen per minute	Rate of formation of benzoic acid divided by the total peroxide concentration
3.4	11.6	0.70	2.06
4.5	14.6	.80	1.78
5.0	15.4	.90	1.80
5.5	20.0	.95	1.73
5.7	23.6	1.00	1.75
5.8	25.6	1.02	1.76
5.7	27.7	1.05	1.84
5.6	29.8	1.03	1.84
5.5	31.8	1.02	1.83
5.4	34.9	1.00	1.85

either Figs. 2 and 3 or Tables IV and V shows that the oxidation of benzaldehyde by the peroxides is much faster in the presence than in the absence of benzoic acid, but that only a small amount of the acid is required to obtain the maximum rate. When the autoxidation is started in the absence of benzoic acid the slowness of the formation of benzoic acid permits the accumulation of peroxides over the steady state concentration. This accounts for the marked maximum in curve 3 of Fig. 2. The excess of peroxide, however, is not the original peroxide formed, for, even after sufficient benzoic acid is present, this peroxide is a less effective oxidizer than that formed in the presence of benzoic acid. This is to be seen by comparing the last columns of Tables IV and V, in which the rates of formation of benzoic acid divided by the peroxide concentration are shown. The less reactive peroxide is probably perbenzoic acid, which is formed from another peroxide by a reaction that is inhibited in the presence of benzoic acid. The simplest explanation of this inhibition is that the precursor of perbenzoic acid combines with benzoic acid, forming a compound which readily oxidizes benzaldehyde.

When no benzoic acid is present initially perbenzoic acid is formed and only slowly oxidizes benzaldehyde to benzoic acid which, in turn, inhibits the formation of more perbenzoic acid, the peroxide–benzoic acid compound being formed instead. At the point where the rate of formation of benzoic acid is greatest the ratio between this rate and the peroxide concentration is small because a large fraction of the peroxide is in a less reactive form. As the less reactive peroxide is now being used up faster than it is produced, the peroxides become richer in the peroxide–benzoic acid compound. Hence the values in the last column of Table IV increase, approaching the more constant values of Table V.

When benzoic acid is present initially, very little perbenzoic acid is formed and the peroxides rapidly reach a steady state concentration and a constant composition. This steady state concentration is practically constant when the oxygen pressure is constant and the concentration of benzaldehyde changes only slowly. The change in the concentration of benzaldehyde probably affects the rates of formation and removal of the peroxide in the same way. The values shown in the third and fourth columns of Table V are, consequently, practically constant after the first few minutes.

When benzoic acid is present initially, the rate of absorption of oxygen does not continue to decrease after the first few minutes but the rate is less than the initial rate in the absence of benzoic acid. The peroxide–benzoic acid compound is presumably an inhibitor. This action may be explained if it is assumed that activated benzaldehyde molecules are links in the chain for the absorption of oxygen, and that they can react with the peroxide–benzoic acid complex. The constancy of the rate of absorption of oxygen,

therefore, depends upon the constancy of the steady state concentration of the peroxide–benzoic acid compound. We have ignored the fact that the initial absorption rate is smaller in the presence than in the absence of benzoic acid. This observation is probably not significant, because only after many crystallizations is benzoic acid sufficiently pure that its addition does not produce a distinct induction period, and it is not certain that this influence is entirely absent.

Finally, in the absence of initial benzoic acid, the absorption rate may fall below the constant rate obtained with initial benzoic acid. There is, probably, another reaction path which produces a poison, but which is prevented when a reaction is started in the presence of benzoic acid. It may be seen by comparing the total absorption points of Fig. 3 with those of Fig. 2 that the reactions of the benzaldehyde–benzoic acid mixture were much more reproducible in rate than those started with pure benzaldehyde. This marked difference may be the result of an uncontrolled production of a poison in the latter case. Conditions that favor such a side reaction would rapidly bring the autoxidation to a stop. We have occasionally observed this phenomenon in reactions whose rate at the start was normal but, in a few minutes, decreased below the limits of observation. Rieff[9] shows some similar curves and attributes the phenomenon to extreme dryness. Kuhn and Meyer[10] have obtained inactive benzaldehyde and attribute its inactivity to freedom from traces of catalysts. We did not succeed in obtaining these aborted reactions at will, but we found no such examples in reactions started in the presence of benzoic acid.

Summary

The distribution of oxygen between peroxides and benzoic acid during its absorption by purified benzaldehyde and by benzaldehyde containing benzoic acid has been quantitatively determined. The reaction is of the first order with respect to oxygen and consists of a series of reactions which involve the formation of peroxides from benzaldehyde and oxygen and the subsequent reaction of these with benzaldehyde to produce benzoic acid.

Certain respects in which the reaction differs from simple, consecutive reactions are due to the autocatalytic nature of the formation of benzoic acid. In the reactions started in the absence of benzoic acid, the peroxides accumulate at first but later their concentration decreases to that of a steady state. In reactions started in the presence of benzoic acid the concentration of peroxides quickly reaches an almost constant value. In both cases the reactions tend to become identical. A mechanism to account for these results has been proposed.

BERKELEY, CALIFORNIA

[9] Rieff, THIS JOURNAL, **48**, 2893 (1926).

[10] Kuhn and Meyer, *Naturwissenschaften*, **16**, 1028 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

GERMANIUM. XXXIX. THE POLYMORPHISM OF GERMANIUM DIOXIDE[1]

BY A. W. LAUBENGAYER AND D. S. MORTON

RECEIVED FEBRUARY 12, 1932 PUBLISHED JUNE 6, 1932

Introduction

Preceding Observations on Germanium Dioxide.—Germanium dioxide, as it is ordinarily prepared by the hydrolysis of the germanium tetrahalides or the alkali germanates, forms an exceedingly fine-grained precipitate, the individual particles of which do not reveal any definite structure under the microscope at the highest attainable resolving power. However, when examined by powder x-ray diffraction methods, the solid gives a well-defined pattern and therefore is microcrystalline. If the dioxide is formed under conditions more favorable for crystal growth, grains of appreciable size may be obtained. According to Goldschmidt,[2] germanium dioxide obtained by crystallization from its aqueous solution yields trigonal crystals that closely resemble the trigonal-trapezohedral low-quartz. Zachariasen[3] has investigated the crystal structure of this form of germanium dioxide by powder x-ray diffraction methods and confirms Goldschmidt's observations. The fundamental lattice is simple hexagonal.

Crystalline germanium dioxide may also be secured by the devitrification of the glass obtained when the fused dioxide solidifies. Müller[4] has shown that crystals prepared in this way give the same x-ray diffraction patterns as the crystals produced by hydrolysis of the tetrachloride or by crystallization from aqueous solution and, therefore, are the same crystalline modification. This form of germanium dioxide is somewhat soluble in water, and hence has been termed "soluble" germanium dioxide.

Müller and Blank[5] announced the discovery of a second crystalline modification, designated by them as "insoluble" germanium dioxide. They prepared the new form by igniting at about 380° the residue left upon evaporation of an aqueous solution of the oxide. Conversion to the insoluble form was never complete and the yield secured depended upon the conditions of evaporation of the solution and upon the time and temperature of ignition of the residue. Higher or lower temperatures of ignition decreased the yield, and it increased with time of ignition at a decreasing rate, approaching a maximum of about 15%. This

[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by D. S. Morton in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Goldschmidt, *Naturwissenschaften*, **14**, 295 (1926).

[3] Zachariasen, *Z. Krist.*, **67**, 226 (1928).

[4] Müller, *Proc. Am. Phil. Soc.*, **65**, 183 (1926).

[5] Müller and Blank, THIS JOURNAL, **46**, 2358 (1924).

insoluble form of germanium dioxide is, according to Müller, extraordinarily inert toward substances which readily act on the oxide in its usual condition. Besides being virtually insoluble in water, it does not react with hydrochloric or hydrofluoric acid. It yields a powder x-ray diffraction pattern completely different from that of the "insoluble" modification. No attempt was made by Müller to interpret the diffraction patterns in terms of crystal structure.

It has been established, therefore, by preceding investigations that germanium dioxide can crystallize in at least two different modifications. One of these is moderately soluble in water and is chemically reactive, while the other is practically insoluble in water and is chemically inert. As regards the stability relations, it follows from the data on solubility that the insoluble form is stable at ordinary temperatures, but there is no conclusive evidence as to whether soluble germanium dioxide is monotropic or enantiotropic with respect to the insoluble form. No convenient method for preparing the insoluble modification has been worked out, and its properties have been determined only incompletely.

Object of this Investigation.—In the present investigation a systematic study of germanium dioxide as a one-component system has been undertaken, involving a determination of the phases occurring, their equilibrium relations and their more important properties.

Experimental

I. Materials

The germanium dioxide was prepared by the hydrolysis of redistilled germanium tetrachloride. It was ignited to remove water and traces of chloride and spectroscopic examination[6] showed that the total sum of metallic impurities present was less than 0.01%.

Fused Germanium Dioxide.—Fused germanium dioxide was made by the method described by Dennis and Laubengayer.[7]

Soluble Crystalline Germanium Dioxide.—The soluble crystalline modification was prepared by heating fused germanium dioxide at 1080° for four hours to ensure complete devitrification. The product appeared entirely crystalline and homogeneous under the microscope.

Insoluble Crystalline Germanium Dioxide.—This form was prepared according to Müller's method[5] which was, however, found to be tedious and to yield poorly formed crystals that were so small as to render difficult their identification under the microscope. Preliminary experiments showed that rapid inversion of the soluble dioxide to the insoluble modification could be secured by a hydrothermal method that produced well-formed crystals. Large samples were prepared by this procedure, which will be described later.

These three forms of germanium dioxide were examined and their properties were determined in order to gain familiarity with their distinguishing features, so that they could be identified when they appeared in the course of the investigation.

[6] The authors wish to acknowledge the kind assistance of Professor J. Papish, who made frequent spectroscopic examinations of the samples.

[7] Dennis and Laubengayer, *J. Phys. Chem.*, **30**, 1510 (1926).

II. Determination of Stability Relationships

Procedure.—The facts already known regarding the behavior of germanium dioxide, and the close analogy between this oxide and silica, made it evident that the changes in the system are of the sluggish type. Therefore the common dynamic methods for the determination of monovariant equilibrium could not be employed. In the static method the system is maintained at a suitable constant temperature long enough to assure the attainment of equilibrium, and then is rapidly quenched to a temperature where the rate of progress toward equilibrium is very slow. The phase distribution corresponding to equilibrium at the higher temperature is thereby preserved and can be examined at leisure. Upon trial, this static or quenching method was found to be satisfactory for the study of germanium dioxide.

Persistence of the Modifications in the Pure State.—In order to obtain some information about the readiness with which the various forms of germanium dioxide tend to invert, samples of the soluble crystalline dioxide and of the insoluble dioxide were heated for forty-eight hour periods at 485, 620, 695, 810, 970 and 1050° (±20°). The samples were quenched by dipping the crucibles in ice water and were examined for signs of inversion. In every instance both forms of the oxide persisted unmodified. The inversions are very sluggish and do not proceed with appreciable velocity in the pure state up to at least 1050°. In similar experiments with the fused oxide it was found that complete crystallization occurred at 660°, incipient crystallization at 620°, and no crystallization at 550°. The crystals were invariably the soluble modification.

Inversions by the Hydrothermal Quenching Method.—To secure the inversion of a modification of a substance that, although unstable, persists indefinitely in the pure, dry state, it is necessary to use a catalytically acting solvent or flux, in the presence of which a more rapid approach to equilibrium occurs. In investigations on silica and the silicates the hydrothermal method, employing as the inversion catalyzer water or an aqueous solution confined in a vapor-tight bomb, has been shown to be effective.[8] This method was therefore tried with germanium dioxide.

The bomb and furnace were similar to those developed at the Geophysical Laboratory at Washington.[9] The bomb, however, was modified according to the simpler design described by Friedrichs.[10] It was made of stainless steel and could be used at temperatures up to 550° without showing appreciable attack. At higher temperatures the threads had a tendency to weld together, even when lubricated with finely powdered graphite, so that the bomb could not be opened.

[8] Fenner, *J. Wash. Acad. Sci.*, **2**, 471 (1912).

[9] Morey and Fenner, THIS JOURNAL, **36**, 215 (1914).

[10] Friedrichs, *Sprechsaal*, **61**, 282 (1928).

Preliminary tests of this new method showed that the soluble crystalline form of germanium dioxide was rapidly converted to the insoluble modification when heated in the bomb in the presence of water at 350°. Large samples of insoluble dioxide were then prepared. From 8 to 10 g. of soluble germanium dioxide and 8 g. of water were placed in a platinum crucible which was covered with platinum foil and was set in the bomb. The sealed bomb was heated for four or five days at about 350° and then was cooled rapidly to room temperature. The product was found to be discolored by iron oxide, which was removed by digesting the germanium dioxide on a steam-bath with successive portions of 6 *N* hydrochloric acid. The residue was washed free from acid with hot water, was dried for fifteen hours at 500° and was weighed. Table I gives the data for three preparations.

TABLE I

PREPARATION OF INSOLUBLE GERMANIUM DIOXIDE BY THE HYDROTHERMAL METHOD

Preparation	Soluble oxide, g.	Time heated, hours	Temp., °C. (±20°)	Product g.	Yield, %
1	8.023	95	350	7.818	97.5
2	10.481	117	355	10.338	98.6
3	10.407	115	360	9.908	95.2
Total	28.911			28.064	97.1

Spectroscopic examination showed that the product was very pure germanium dioxide. To test for the completeness of inversion to the insoluble form, weighed portions of the material were digested in covered platinum crucibles on the steam-bath with concentrated hydrofluoric acid for one hour. No appreciable weight of the sample dissolved. Microscopic examination also demonstrated that the product was a homogeneous preparation of insoluble crystalline germanium dioxide. The inversion was undoubtedly complete, the 97% yield being due to the loss of slight amounts of the insoluble dioxide in suspension when the product was washed by decantation.

The hydrothermal method of preparing insoluble germanium dioxide possesses several advantages over the method of Müller. By its use a large amount of soluble oxide can be transformed directly and quantitatively into the insoluble modification. Moreover, the product is composed of crystals of resolvable size which can be identified readily under the microscope. Further experience indicated that forty-eight hours' heating is sufficient for effecting complete inversion.

To determine the phase stable at a given temperature by the hydrothermal method, 0.1-g. samples of soluble germanium dioxide, insoluble germanium dioxide and fused germanium dioxide were each placed, with 1.5 cc. of water, in small platinum thimbles which were stacked one above the other in the bomb. The sealed bomb was held at the desired tempera-

ture for forty-eight hours. It was then quenched in ice water and the resulting products, after being dried at 120°, were examined with the microscope to ascertain the nature and relative amounts of the phases present. Identification of the various forms was based primarily on their refractive indices, namely, 1.608 for the fused dioxide, 1.70 for the soluble dioxide and 1.99+ for the insoluble dioxide. The identifications were also checked by testing the solubility of the specimen with hydrofluoric acid. The range between 140 and 550° was investigated and the results are given in Table II.

TABLE II

INVERSIONS BY HYDROTHERMAL METHOD

Inversion catalyzer, water Time, 48 hours

Temp., °C. (±10°)	Form of GeO_2 used: Soluble	Insoluble	Fused
	Forms present in product		
140	S	I	S, F
180	I	I	S
220	I	I	S, I
260	I	I	I
320	I	I	I
345	I	I	I
450	I	I	I
550	I	I	I

NOTATION: S, soluble crystalline GeO_2; I, insoluble crystalline GeO_2; F, fused GeO_2. The more abundant form is listed first.

From these data it is evident that throughout the range studied the insoluble modification of germanium dioxide is stable since it remains unchanged while the soluble and fused dioxide tend to invert to it. At 180° and above, this hydrothermally catalyzed inversion of the soluble crystalline form is completed in forty-eight hours or less. The crystals of insoluble oxide formed, while always very small, are larger the higher the temperature of the inversion. In accordance with Ostwald's rule, the metastable soluble crystalline modification appears as an intermediate product in the process of conversion of the fused oxide to the insoluble oxide at 180 and 220°. No new crystalline form was observed in any of the preparations.

Inversions by the Fusion-Quenching Method.—Since the bomb could not be employed above 550°, it was necessary to use another experimental method to explore the temperature range up to the melting point of germanium dioxide, which was known to be somewhat above 1100°. The addition of a suitable fused salt has been found to accelerate certain sluggish inversions sufficiently to make the equilibrium relations readily ascertainable by a quenching method. Fenner[11] employed sodium tungstate for this purpose in working out the stability diagram for silica,

[11] Fenner, *Am. J. Sci.*, **36**, 331 (1913).

and van Nieuwenburg and de Nooijer[12] determined the efficiency of a large number of substances for catalyzing the inversion of quartz to tridymite at 1000°.

To ascertain the best catalyst to use for studying the inversions of germanium dioxide in the range of 550 to 1100°, a series of preliminary experiments with sodium tungstate, sodium molybdate, potassium bisulfate, anhydrous magnesium chloride, boric acid and the alkali chlorides were tried. The eutectic melt mixture of potassium chloride and lithium chloride, containing 44.6% by weight of lithium chloride, and melting at 358°, was found to be the most satisfactory. Using this flux a systematic examination of the stability relations of the various forms of the oxide between 550 and 1100° was made according to the following procedure.

Mixtures of each modification of germanium dioxide and the catalyzing flux were prepared in platinum crucibles by evaporating to dryness a suspension of the oxide in 2–3 cc. of water containing the requisite amount of chlorides. The covered crucibles were held at the desired temperature in a muffle furnace which could be maintained constant within ±10° for periods varying from one-half to thirty-six hours, according to the temperature employed. In some instances it was necessary to carry out several experiments at a single temperature before a satisfactory combination of conditions with respect to relative amounts of oxide, flux and time of heating was obtained. Of the conditions tried, those reported in Table III were the most effective. After the ignition the samples were quenched in ice water and were washed free from chlorides with hot water. The phases present were ascertained by examination under the microscope and by determination of their solubility in hydrofluoric acid.

TABLE III

INVERSIONS BY FUSION METHOD

Flux: 55.4% KCl, 44.6% LiCl

Experiment	GeO_2, g.	Flux, g.	Time, hours	Temp., °C. (±10°)	Form of oxide used: Soluble	Insoluble	Fused — Forms present in product
1	0.05	0.10	36	500	S, I	I	S, F, I
2	.05	.05	18	600	S, I	I	S, I
3	.05	.02	6	700	S, I	I	S, I
4	.05	.005	1	800	S, I	I	I
5	.05	.0005	0.5	905	I	I	I
6	.05	.0005	0.5	980	I, S	I	I
7	.05	.0005	0.5	1020	S, I	I	S, I
8	.05	.0005	0.5	1060	S	I, S	S

These data show that the two crystalline modifications of germanium dioxide are enantiotropic with the reversible inversion point lying between

[12] Van Nieuwenburg and de Nooijer, *Rec. trav. chim.*, **47**, 627 (1928).

1020 and 1060°. At 1020°, and below, the insoluble form persists unaltered, while the soluble crystals and the glass are both more or less completely transformed to it. At 1060°, on the contrary, the insoluble oxide, as well as the fused oxide, invert into the soluble crystalline modification while the latter undergoes no change. The fused oxide, at temperatures at which the insoluble modification is stable, does not as a rule pass directly into the insoluble form, but yields the metastable soluble crystals as an intermediate phase in accordance with Ostwald's law of successive reactions.

In order to fix the temperature of the inversion point more closely, an improved technique was employed. Mixtures of the various modifications with the potassium chloride–lithium chloride flux were heated in small platinum thimbles suspended in the center of a platinum-wound resistance furnace of the type in use at the Geophysical Laboratory.[13] The thimbles were supported so that the tip of the platinum–platinum-rhodium thermocouple used for measuring the temperature was just above the charge. Throughout the series of experiments the relative amount of catalyst and the time of heating were kept as low as was compatible with decisive results. Fluctuation of the temperature during an experiment never exceeded ±3°. The charges were quenched, washed and dried and the phases present were identified.

TABLE IV

QUENCHING EXPERIMENTS TO LOCATE INVERSION POINT

Flux: 55.4% KCl, 44.6% LiCl

Experiment	GeO_2, g.	Flux, g.	Time, hours	Temp., °C. (±5°)	Form of oxide used: Soluble — Forms present in product	Form of oxide used: Insoluble — Forms present in product
1	0.05	0.0005	0.5	1018	S, I	I
2	.05	.001	2.0	1025	S, I	I
3	.10	.002	2.0	1028	98.4% S[a] 1.6% I	100 % I[a]
4	.10	.002	2.0	1033	S, Trace I	98 % I[a] 2 % S
5	.10	.002	2.0	1038	100 %S[a]	82.5% I[a] 17.5% S
6	.05	.0005	2.0	1040	S	I, S
7	.05	.0005	0.5	1051	S	I, S
8	.10	.001	1.0	1075	S	
9	.10	.001	1.0	1094	S	
10	.10	.001	1.0	1110	Glass	

[a] By weighing residue insoluble in hydrofluoric acid.

It is evident from these data that at 1028° and below, the insoluble germanium dioxide is stable, at 1038° and above the soluble modification is stable, while at 1033° the two forms exist in equilibrium. Allowing for

[13] Shepherd, Rankin and Wright, *Am. J. Sci.*, **28**, 308 (1909).

uncertainties introduced by errors in calibration and temperature measurement, and for the difficulty of deciding the exact point of discontinuity of stability, the inversion point, Insoluble crystalline $GeO_2 \rightleftharpoons$ Soluble crystalline GeO_2, may be concluded to be $1033 \pm 10°$.

Experiment 10 at 1110° yielded a clear glass due to the lowering of the melting point of germanium dioxide by the presence of the flux. Experience with the chloride mixture as a catalyzing flux justifies the belief that it is exceedingly conducive to the transformation of germanium dioxide to the most stable phase. Since in experiments 5 to 9 the soluble crystalline modification persisted unchanged, it may be concluded that this form is stable between 1033° and the stable melting point.

Determination of the Melting Points.—Germanium dioxide has a strong tendency to supercool and superheat and therefore the quenching[14] method for the determination of melting points was used. The procedure consisted, essentially, in holding samples at various different constant temperatures in the vicinity of the melting point, quenching them and observing the phases present. The platinum-wound resistance furnace used for the determination of the inversion point was again employed and was maintained at temperatures constant to ±1°. The data obtained for the two forms of the dioxide are given in Tables V and VI.

TABLE V

DATA FOR MELTING POINT OF SOLUBLE CRYSTALLINE GeO_2

Experiment	Time of heating, hours	Temp., °C. (±3°)	Phases in product
1	2	1107.5	S
2	2	1110.0	S, some glass
3	2	1112.5	S, partly glass
4	2	1115.0	Glass, trace of S
5	2	1117.5	Glass
6	6	1111.0	About half glass, half crystals, the latter much larger than before heating

TABLE VI

DATA FOR MELTING POINT OF INSOLUBLE CRYSTALLINE GeO_2

Experiment	Time of heating, hours	Temp., °C. (±3°)	Phases in product
1	0.5	1077.5	I, glass, S
2	.5	1080.0	Glass, S, I
3	.5	1082.5	Glass, S, I
4	.5	1085.0	Glass, S, trace of I
5	.5	1087.5	Glass, S
6	.5	1090.0	Glass, S

If the melting point of soluble crystalline germanium dioxide be taken as the lowest temperature at which the crystalline phase vanishes, and allowance be made for all possible sources of error in the measurements,

[14] Morey, *J. Wash. Acad. Sci.*, **13**, 326 (1923)

it follows from the data in Table V that the melting point may be reported as 1116 ± 4°. This agrees well with the value 1115 ± 3° reported by Schwartz, Schenk and Giese,[15] who also used the quenching method.

At the melting point of insoluble germanium dioxide both it and the liquid phase are metastable and there is the possibility of melting to metastable glass, of inverting directly to the stable soluble dioxide, or of changing through the glass phase to the stable soluble dioxide. It is possible to determine the metastable melting point of insoluble germanium dioxide because the second and third of these transformations proceed more slowly than the first. In the experiments recorded in Table VI the time of heating was so regulated as to be long enough to realize approximately the metastable equilibrium between liquid and insoluble germanium dioxide, but not long enough to admit of much displacement toward the stable soluble crystalline germanium dioxide. The melting point of insoluble crystalline germanium dioxide may, therefore, be taken as the temperature at which the last traces of insoluble crystals disappeared, or 1086 ± 5°.

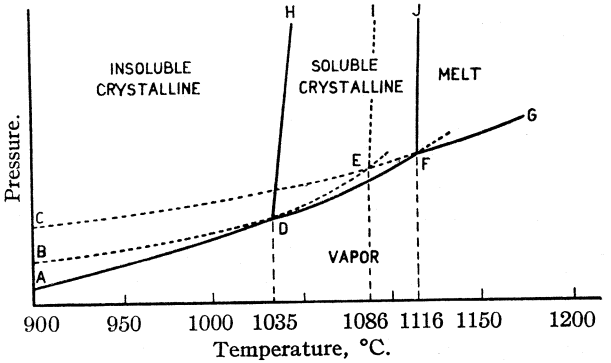


Fig. 1.—Phase diagram of germanium dioxide.

Phase Diagram of Germanium Dioxide.—On the basis of the experimental study it is possible to construct a pressure–temperature diagram of phase equilibria in the one-component system, germanium dioxide. Fig. 1 represents the more important portion of such a diagram. The pressure coördinates have only qualitative significance. Curves ADE, BDF and CEFG are the vapor pressure curves of the insoluble, soluble and fused modifications, respectively. They are constructed on the principle that the form having the lowest vapor pressure is the stable form at a given temperature. The curves intersect at D, the inversion point; F, the melting point of the soluble crystalline modification; and E, the metastable melting point of the insoluble modification. The

[15] Schwartz, Schenk and Giese, *Ber.*, **64**, 364 (1931).

lines DH, EI and FJ represent the probable mode of variation of the inversion point and melting points with pressure. From the relative densities of the three forms, it follows that each of these lines has a positive slope; and unless, as is very unlikely, the heat of inversion is considerably greater than the heat of fusion, line DH makes the greatest angle with the axis of pressures.

Improbability of a Third Crystalline Modification.—From the fact that the soluble crystalline form undergoes no inversion when heated with a flux at temperatures between 1033 and 1090°, and that it persists unchanged at temperatures just below its melting point, we have inferred that no third enantiotropic crystalline modification of germanium dioxide exists. This does not exclude the possibility of a monotropic modification, but, if such a form occurs, it has not appeared in appreciable amount in any of our preparations.

Müller and Blank[5] have postulated the existence of three crystalline modifications of germanium dioxide to explain the fact that only a limited fraction of their "evaporated" oxide can be converted to the insoluble form, no matter how long the material is heated, and the fact that this maximum yield varies with different preparations according to the conditions of evaporation. They suggest that the residue from the evaporation of the aqueous solution is not homogeneous, but contains two soluble modifications, one of which undergoes rapid transformation to the insoluble form while the other inverts very slowly if at all.

The presence of two crystalline modifications, however, was not borne out by the x-ray patterns Müller obtained nor by the patterns secured for similar material in the course of the present investigation, although, according to Müller's theory, from 15 to 20% of the third form should be present.

Another explanation for Müller's results, which does not require the existence of a second soluble crystalline modification, may be suggested. The "evaporated" oxide used in the experiments of Müller and Blank always contained moisture. In view of our own hydrothermal experiments, it appears that this moisture should catalyze the inversion. The inversion will be incomplete because the process stops as soon as the moisture has been expelled. The hypothesis that the presence of moisture is necessary to bring about the inversion may also account for the peculiar form of Müller and Blank's yield–temperature curve, which shows an apparent maximum rate of transformation at 380°. At low temperatures, the rate of inversion is itself small, regardless of the amount of water present. At high temperatures, the excess moisture is expelled before the inversion has progressed very far. At 380° the rates of inversion and of evaporation of the water are so related that the amount of inversion in a given time is a maximum.

It is still necessary to explain why different preparations of the "evaporated" oxide, under identical conditions, show different yields of the insoluble modification, and also why the "hydrolyzed" oxide, which ordinarily contains more water than the "evaporated" variety, is not converted at all upon ignition. It is possible that the "evaporated" oxide, although consisting mainly of the soluble modification, contains also nuclei of the insoluble crystals, formed during the protracted evaporation, which serve as centers of crystallization under conditions favoring a transformation. If these nuclei are sufficiently small, they may be numerous and still escape detection by x-ray analysis, microscopic examination, or solubility tests. The amount of conversion of two different samples, similarly treated, will depend on the comparative number of "insoluble" nuclei initially present in each sample, as well as on the amount of water present. The "hydrolyzed" oxide, having been precipitated from solution by a rapid chemical reaction, may conceivably contain no "insoluble" nuclei whatever.

It is very doubtful whether a third monotropic crystalline modification of germanium dioxide exists. There is no direct evidence of its existence, and the indirect evidence offered by Müller and Blank can, as we have shown, be otherwise interpreted. Recently Schwartz and Huf[16] have reported that solubility measurements for the various forms of germanium dioxide do not warrant the assumption of the existence of a third crystalline modification.

III. Properties of the Crystalline Forms

The existing data concerning the properties of the crystalline modifications of germanium dioxide were so incomplete and, in some cases, so contradictory, that it appeared desirable to determine systematically the more important physical and chemical properties.

Crystal Structure.—Zachariasen's[3] analysis of the crystal structure of the soluble crystalline modification has already been cited in the introduction to this article. A table of sine-squares which we calculated from measurements of x-ray powder diffraction photographs of this form agreed closely with his values.

The crystal structure of the insoluble modification of germanium dioxide was determined[17] entirely from x-ray powder diffraction photographs, taken with a General Electric x-Ray Diffraction Apparatus of the type described by Davey.[18]

[16] Schwartz and Huf, *Z. anorg. allgem. Chem.*, **203**, 188 (1932).

[17] The authors are indebted to Prof. C. C. Murdock, of the Department of Physics, for his kind assistance in obtaining the x-ray patterns and in the solution of the crystal structure.

[18] Davey, *J. Optical Soc. Am.*, **5**, 479 (1921).

It was found that the fundamental lattice is simple tetragonal, with $c/a = 0.649 \pm 0.002$, and that the dimensions of the unit cell are

$$a_0 = 4.395 \pm 0.010 \text{ Å.}, \quad c_0 = 2.852 \pm 0.015 \text{ Å.}$$

The observed interplanar distances corresponding to the first twenty-five lines on the film agreed well with the distances calculated from these parameters.

To correspond to the observed density, 6.239 g./cc., there must be two molecules of GeO_2 in the unit cell. The calculated density is then 6.26 ± 0.06 g./cc.

These data support the hypothesis, already suggested by Zachariasen,[19] that the insoluble modification of GeO_2 has the "rutile" type of structure. In this structure the unit cell is a tetragonal prism, and contains two molecules. The centers of the two metal ions are at (0, 0, 0) and ($1/2$, $1/2$, $1/2$), while those of the four oxygen ions are at (u, u, 0), ($1/2 - u$, $1/2 + u$, $1/2$), ($1/2 + u$, $1/2 - u$, $1/2$) and ($1 - u$, $1 - u$, 0). For rutile, $u = 0.30 \pm 0.01$. The space group is D_{4h}^{14}.

Powder diffraction patterns of insoluble GeO_2 and rutile were photographed beside each other on the same film. The patterns were very similar; for every line in one pattern there was a corresponding line in the other, having, usually, about the same relative intensity. The odd order reflections from the 100, 001 and 201 planes were absent from both patterns.

The theoretical intensities of the lines in the pattern of GeO_2, for an assumed rutile type of structure, were calculated and compared with the experimental values. In the calculations, the general formula for powder patterns,[20]

$$I_{hkl} \propto F^2 s \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \qquad (1)$$

and the atomic scattering powers of O^{2-}, Ti^{4+} and Ge given by James and Brindley,[21] were employed. The intensities were obtained, not by comparing the lines of the pattern of GeO_2 with each other, but by comparing each GeO_2 line with its counterpart in the pattern of rutile, the intensity of which was calculated from the known crystal structure by formula (1). The observed intensities, and those calculated using values of u from 0.26 to 0.34, are listed in Table VII. All values are expressed as percentages of the intensity of the 002 reflection. The lines beyond those listed were, with few exceptions, too faint to allow of accurate estimates of intensity.

The general agreement between calculation and experiment is best

[19] Ref. 3, p. 233.

[20] Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 2d edition, 1931, p. 165.

[21] James and Brindley, *Z. Krist.*, **78**, 470 (1931).

for $u = 0.30$, and appears close enough to confirm the assumption of the rutile type of structure for insoluble GeO_2. Values of u below 0.28, or above 0.32, appear to be excluded: otherwise the 120 line would be invisible or else decidedly more intense than the 400 line.

TABLE VII

COMPARISON OF THE THEORETICAL AND OBSERVED INTENSITIES OF THE LINES IN THE POWDER PATTERN OF INSOLUBLE GeO_2

Obs. spacing, Å.	Indices	Obs. intensity	Calculated intensity				
			$u = 0.26$	0.28	0.30	0.32	0.34
3.10	110	1500	1162	1197	1267	1371	1504
2.390	101	920	1043	929	825	730	647
2.194	200	320	144	158	185	228	287
2.104	111	130	126	118	104	85	65
1.965	120	30	2	13	30	47	56
1.618	121	910	700	759	799	812	788
1.556	220	220	268	252	224	194	168
1.424	002	100	100	100	100	100	100
1.389	130	160	203	191	172	152	139
1.299	301 112	660[a]	348	392	433	464	479
1.195	202	40	59	62	69	80	93
1.117	231	100	172	140	125	128	147
1.096	400	50	76	68	55	41	31

[a] Probably too high. The intensity of this compound line is really not comparable with that of the corresponding line in the pattern of rutile, because the component lines in the case of rutile do not fully coincide, on account of its lower axial ratio.

While the sequence of intensities of the lines in the patterns of GeO_2 and of rutile was, for the most part, the same, there were certain exceptions. Of these, the most striking was in the case of the lines 200, 111 and 120. For GeO_2, $I_{200} > I_{111} > I_{120}$; for TiO_2, $I_{111} > I_{120} > I_{200}$. This difference in order is accounted for by the difference in the scattering powers of the titanium and germanium ions, and does not necessitate any difference in the ionic arrangement. This is shown in Table VIII, in which the values of F^2s (formula (1)), for a rutile structure with $u = 0.30$ are given.

TABLE VIII

Reflection	F^2s	
	GeO_2	TiO_2
200	3615	522
111	2216	2413
120	740	810

It is concluded that the arrangement of ions in the unit cell of insoluble GeO_2 is of the rutile type, and that the value of the parameter u is 0.30 $\pm$ 0.02.

Drawings of this structure are given by Wyckoff.[22] Each germanium ion is surrounded by six oxygen ions, whose centers lie at the corners of a somewhat distorted octahedron. The shortest Ge—O distance is 1.86 Å.;

[22] Ref. 20, p. 231.

and the effective radius of the Ge^{4+} ion, on the basis of 1.32 Å. for the radius of the oxygen,[23] is 0.54 Å.

Optical and Crystallographic Properties.—Specially selected, well-defined crystals of both modifications were kindly examined for us under the microscope by Professor C. W. Mason, who reports on them as follows:

"**Soluble GeO_2.**—Well-formed approximately cubical crystals, which are rhombohedra of the hexagonal system. They show strong double refraction and symmetrical extinction, and yield uniaxial positive interference figures. $\omega = 1.695 \pm 0.005$; $\epsilon = 1.735 \pm 0.005$.

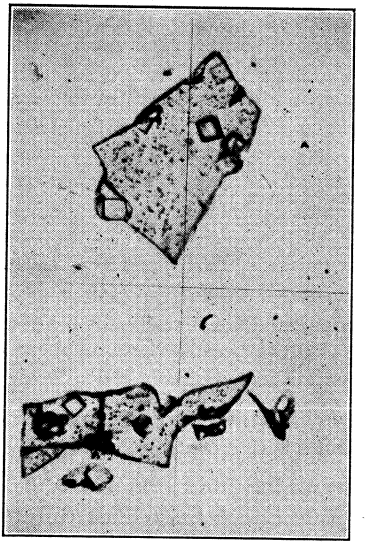


Fig. 2.—Soluble crystalline germanium dioxide.

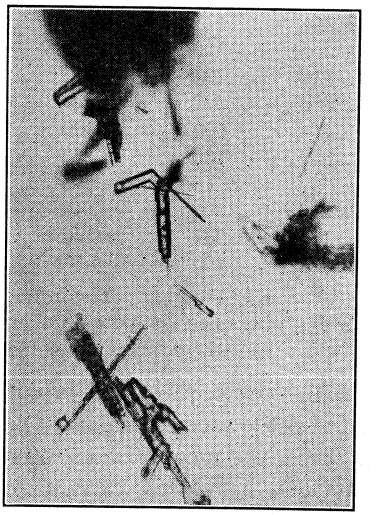


Fig. 3.—Insoluble crystalline germanium dioxide.

"**Insoluble GeO_2.**—Clusters and rosets of prisms and lath-shaped forms, also very fine needles. Some knee turns. The surfaces of the larger crystals are rough and apparently eroded. End faces of definite form are not evident. Double refraction is strong, with the sign of elongation and parallel extinction exhibited by all side views of the prisms. The crystals belong to the tetragonal system. $\omega = 1.99$, $\epsilon = 2.05$–2.10 (estimated)."

Photomicrographs of the samples examined are reproduced in Figs. 2 and 3. The crystals of the soluble oxide, which are embedded in the fused oxide, were produced by heating the insoluble modification for two hours at 1100°. It would appear that the insoluble oxide melted almost immediately; but the melt was unstable with respect to the soluble modification, which accordingly crystallized out.

[23] Goldschmidt, "Geochemische Verteilungsgesetze," Oslo, Vol. VII, 1926, p. 15.

The specimen of insoluble germanium dioxide shown in Fig. 3 was isolated by extracting with hydrofluoric acid the product of heating the soluble oxide with 1% of its weight of potassium chloride–lithium chloride mixture at 1020°. It contained numerous elbow twins, like the one appearing in the photograph, with an angle of 114 ± 1° between the two members. On the assumption that in these twins the components lie on 010 faces and are joined on the 011 plane, the axial ratio c/a calculated from this angle is 0.65 ± 0.015, thus confirming the x-ray value, 0.649. Contact twins of this type are often observed on rutile and cassiterite.[24]

Density.—The values for the density of soluble crystalline germanium dioxide given by different investigators are very discordant, probably due to the difficulty in securing well-crystallized, homogeneous samples.

The densities of our preparations of soluble and insoluble crystalline germanium dioxide were determined pycnometrically, using toluene as the immersing liquid. The samples were dried to constant weight at 950° immediately before each determination. All weighings were corrected to vacuum. The results of duplicate determinations are given together with the value secured by x-ray methods by Zachariasen for the soluble oxide and that obtained by x-ray methods in the present investigation for insoluble germanium dioxide.

TABLE IX

Modification	Density at 25° (1)	(2)	Av.	x-Ray density
Soluble crystalline GeO_2	4.233	4.224	4.228	4.28
Insoluble crystalline GeO_2	6.234	6.244	6.239	6.26

It will be noticed that in both cases the difference between the pycnometric and x-ray densities is slight and is in the expected direction, inasmuch as the value measured directly tends to be lowered by the presence of voids in or between the crystals. The samples used by the authors in the determinations cited above consisted of well-formed crystals of appreciable size. When less perfectly crystallized material was used the results were always lower.

Solubility in Water at 25°.—Solubility determinations were made by agitating the solid with water in a Pyrex glass flask in a thermostat until equilibrium was established and then evaporating a given weight of the saturated solution to dryness and weighing the residue; 4.53 g. of soluble crystalline germanium dioxide was found to dissolve in 1000 g. of water at 25°. This is in good agreement with the value 4.47 g. per 1000 g. of water at 25° reported by Pugh.[25] The insoluble crystalline modification was not appreciably soluble.

[24] Groth, "Elemente der physikalischen und chemischen Krystallographie," 1921, p. 200.

[25] Pugh, *J. Chem. Soc.*, 1537 (1929).

Chemical Properties.—Samples of 0.2 g. of the insoluble crystalline oxide, previously dried at 950°, were digested on the steam-bath with 10 cc. of each of the following reagents: 25 *N* hydrofluoric acid, 12 *N* hydrochloric acid, 36 *N* sulfuric acid and 5 *N* sodium hydroxide. After one hour the undissolved residue was separated from the liquid by decantation and filtration, and was washed, ignited and weighed. There was no appreciable solution in any of the three acids, but in the case of the 5 *N* sodium hydroxide, the losses in weight of the sample, in two determinations, were 16.8 and 17.8%, respectively. These figures were corroborated by determining the amount of germanium dioxide in the filtrate and washings by the method of Johnson and Dennis.[26] Contrary to the statement of Müller and Blank[27] the insoluble oxide is not wholly unattacked by hot alkaline solutions. The rate of solution, however, is slow compared with that of the soluble crystalline form.

In similar tests, the soluble modification was rapidly attacked by 25 *N* hydrofluoric acid, 12 *N* hydrochloric acid and 5 *N* sodium hydroxide, but scarcely at all by 36 *N* sulfuric acid.

The insoluble oxide reacted readily when fused with ten times its weight of sodium hydroxide at 550°, or with five times its weight of sodium carbonate at 900° or above. In both cases the melt was completely soluble in water.

To facilitate comparison, the properties of the two crystalline forms and of the glass are tabulated in Table X. The information on the glass is as given by Dennis.[28]

TABLE X

PROPERTIES OF GERMANIUM DIOXIDE

	Insoluble crystalline	Soluble crystalline	Glass
Crystal system	Tetragonal	Hexagonal	Amorphous
Crystal structural type	Rutile	Low-quartz	
Density at 25°, g./cc.	6.239	4.228	3.637
x-Ray density, g./cc.	6.26	4.28	
Indices of refraction	$\omega = 1.99$	$\omega = 1.695$	
	$\epsilon = 2.05$–2.10	$\epsilon = 1.735$	1.607
Inversion point	1033 ± 10°	1033 ± 10°	
Melting point	1086 ± 5°	116 ± 4°	
Solubility at 25°, g./1000 g. H_2O	Insoluble	4.53	5.184 g./l. (at 30°)
Action of HF	None	Reacts, giving H_2GeF_6	Reacts, giving H_2GeF_6
Action of HCl	None	Reacts, giving $GeCl_4$	Reacts, giving $GeCl_4$
Action of 5 *N* NaOH at 100°	Slowly dissolves	Rapidly dissolves	Rapidly dissolves

[26] Johnson and Dennis, THIS JOURNAL, **47**, 790 (1925).

[27] Ref. 5, p. 2359.

[28] Dennis, *Z. anorg. allgem. Chem.*, **174**, 97–141 (1928).

Discussion

Morphotropic Relationships.—A classification of the dioxides of the elements of group IV according to crystal structures is given in Table XI. The soluble or high-temperature modification of germanium dioxide is isomorphous with low-quartz, while the insoluble or low-temperature modification is isomorphous with the dioxides of tin and lead.

TABLE XI

CRYSTAL STRUCTURES OF DIOXIDES OF GROUP IV

Hexagonal low-quartz structure	Tetragonal rutile structure
Low-quartz, SiO_2 (below 575°)	Insoluble GeO_2 (below 1033°)
Soluble GeO_2 (above 1033°)	Cassiterite, SnO_2
	Plattnerite, PbO_2

It is thus evident that the effect on the crystal structure of germanium dioxide of raising the temperature is the same as that of substituting a small cation for the germanium.

The occurrence of two modifications of germanium dioxide is in accordance with Goldschmidt's[29] views on the relation of the crystal structures of compounds of the type AX_2 to the ratio of the ionic radii. The geometrical boundary between structures with coördination numbers 2 and 4, such as the low-quartz type, and those with coördination numbers 3 and 6, such as the rutile type, is at $r_A/r_X = 0.414$. Taking our value of 0.54 Å. for the radius of the germanium ion, and Goldschmidt's value of 1.32 Å. for that of the oxygen ion, $r_{Ge}/r_0 = 0.409$. That is, the ionic radial ratio for germanium dioxide is so close to the theoretical boundary between the two structural types that the compound can assume one structure or the other, depending on external conditions of temperature and pressure.

The value of 0.44 Å. given by Goldschmidt for the radius of the germanium ion is evidently too low. It is to be noted that Pauling's calculated value is 0.53 Å.

Summary

1. The polymorphism of germanium dioxide is confirmed and methods of preparing the soluble and insoluble modifications in a well-crystallized condition are described.

2. Inversion from either crystalline modification to the other is shown to be of the sluggish type. By the use of the quenching method with an accelerating flux, it is shown that the two modifications are enantiotropic, with the inversion point at 1033 ± 10°.

3. Using the quenching method, the stable melting point of the soluble modification, 1116 ± 4°, and the metastable melting point of the insoluble modification, 1086 ± 5°, have been determined.

[29] Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

4. The phase relations in the one-component system germanium dioxide are represented diagrammatically and are discussed.

5. From a consideration of the available evidence, it is concluded that a third crystalline modification of germanium dioxide probably does not exist.

6. The crystal structure of the insoluble modification, and the density, solubility, indices of refraction and chemical activity of both modifications have been determined.

7. A discussion of the crystallo-chemical relationships of germanium dioxide to the dioxides of the other elements of the fourth periodic group is submitted.

ITHACA, N. Y.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 293]

THE SPARK-IN-FLAME METHOD OF SPECTROGRAPHIC ANALYSIS AND A STUDY OF THE MUTUAL EFFECTS OF ELEMENTS ON ONE ANOTHER'S EMISSION[1]

BY RALPH HULTGREN

RECEIVED FEBRUARY 15, 1932 PUBLISHED JUNE 6, 1932

Introduction

In recent years the development of methods for the use of the spectrograph as an instrument for the quantitative as well as qualitative chemical determination of elements has proceeded to such an extent that they may now be regarded as suitable for application to many microchemical problems. While spectrographic methods cannot in general compete with ordinary chemical quantitative analysis in point of accuracy, they possess two important advantages which make them of great value in many special cases. These are great sensitivity, which permits of the semi-quantitative estimation of amounts of material too small to be analyzed by other methods, and the great rapidity with which an analysis can be conducted. For details of procedure, accuracy of estimation, etc., the reader is referred to the literature.[2]

The three principal means of exciting emission spectra which have been used in quantitative analysis are the electric arc, the spark and the flame. The arc and spark methods combine the advantages of a high and to some extent controllable excitation with certain drawbacks. While the high

[1] Original manuscript received August 19, 1931.

[2] F. Löwe, "Handbuch der Physik," **21**, 663 (1929); H. Lundegårdh, "Die quantitative Spektralanalyse der Elemente," G. Fischer, Jena, 1929; Eugen Schweitzer, *Z. anorg. Chem.*, **164**, 127 (1927); Walter Gerlach, *ibid.*, **142**, 383 (1925); A. de Gramont, *Bull. soc. chim.*, **33**, 1693 (1923).

excitation makes the method applicable to a large number of elements, and gives a great sensitivity, the difficulty of uniformly introducing representative samples of the material to be analyzed into the spark or arc gases, and the fact that the emission of one element is not independent of the other elements present, lead to some difficulties. These do not seem to be serious in the cases to which the arc and spark methods are usually applied, that is, in the estimation of traces of impurity in a large and nearly constant amount of some other substance, but they impose serious limitations in case that all of the substances in the unknown samples vary largely in relative amounts. The flame method, while very reproducible and nearly free from the objections just cited,[2] is limited in applicability to those few elements which have relatively low excitation potentials.

Purpose of the Investigation.—It was the object of the work here described to devise a method of spectroscopic analysis which would retain the advantage of the flame method but overcome some of its limitations by allowing a higher excitation. It was further proposed to study the mutual effects of some elements on each other's emission with a view toward finding conditions under which these are small, so that unknown samples containing several elements might be analyzed without extensive calibration experiments.

Description of Method and Apparatus

The Method.—After some preliminary experiments the following method was found promising. The difficulties inherent in the ordinary spark methods of vaporizing representative portions of the sample to be analyzed were overcome by atomizing solutions of the sample into a hot flame, in the customary way. The excitation in the resulting gases was then increased by passing through them a condensed discharge.

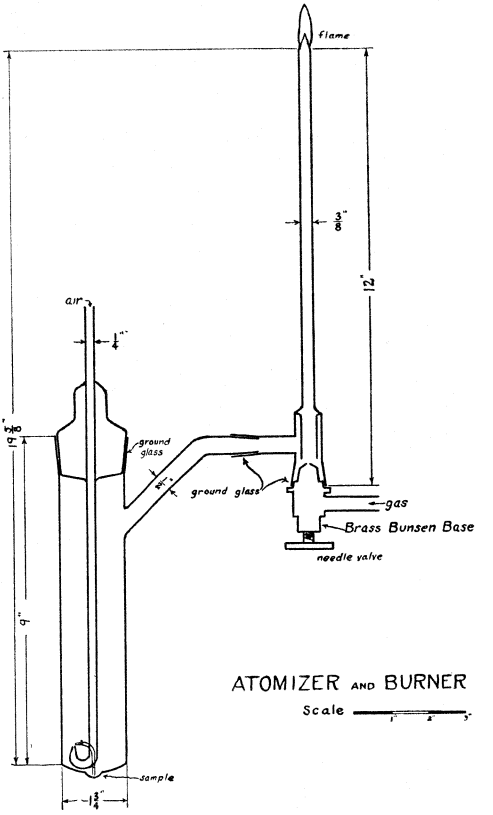


Fig. 1.—Atomizer and burner used for introduction of sample into flame.

The Burner and Atomizer.—Figure 1, which represents the burner and atomizer, is self-explanatory. All parts were of Pyrex glass except the jet admitting gas into the

burner, which was of brass. The design was such as to yield a steady flame and to introduce as large a quantity of solution as possible into the flame gases in finely divided drops. Any large drops produced by the spray deposit on the walls of the atomizer vessel and run back quickly, reducing the volume of solution necessary for an analysis to about 3 cc.

The Spark.—The electrical circuit is shown in Fig. 2. The transformer finally used was a 2 k.v.a. American transformer operating on 220 volts and yielding 25,000 volts in the secondary. With this equipment an exposure time of one minute was usually sufficient. A smaller transformer gave nearly as good results with a longer exposure.

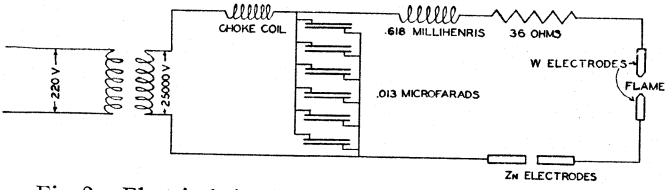


Fig. 2.—Electrical circuit for production of spark-in-flame.

The condenser consisted of 30.5 × 35.6 cm. plates of heavy window glass on both sides of which 25.4 × 30.5 cm. sheets of copper foil were cemented with shellac. Six plates were used and the capacity measured by a comparison method was found to be 0.013 microfarad. The inductance consisted of copper wire wound on three Pyrex glass cylinders covered with friction tape. The calculated inductance was 0.618 millihenris. With the combination of inductance and capacity given, the air lines were eliminated in the spark, and the intensity of the general background was not disturbing.

It will be noted in the diagram that an auxiliary spark gap and a fixed resistance were included in the secondary circuit. The former was found desirable since in its absence breakdown occurs at a very low potential due to the high conductivity of the flame gases. The latter serve to minimize variations due to changes in the conductivity of the flame when varying amounts of elements of low ionization potential were introduced into it, as shown in Table I.

TABLE I

EFFECT OF RESISTANCE WIRE, IN SERIES WITH SPARK, ON SECONDARY CURRENT

Solution used for sample	Secondary current	
	Without resistance wire	With 8′ 4″ res. wire (54 ohms)
Distilled water	3.05	1.58
2 Molal NaCl	1.3	1.5

The Flame.—The fuel in the flame was hydrogen gas saturated with acetone vapor, which gave a very stable flame little affected by the introduction of large amounts of foreign substances. The city gas available is a natural gas and was found quite unsuitable since it burns with a very unstable flame. It is probable, however, that most types of manufactured city gas would work satisfactorily without modification.

The Electrodes.—It was found possible in the following way to produce a spark which over a fairly wide region in its center was completely free from any lines due to the material of the electrodes. Tungsten electrodes 10–12 mm. apart were used, and these projected slightly into the flame from opposite sides. The tungsten vapor evolved is swept away by the flame gases and does not penetrate into the center of the flame. The spark was always passed just above the blue cone of the flame. Tungsten lines are apt to appear if the spark is too far above the cone. No improvement in sensitivity

was noted with closer electrodes, but tungsten lines appeared. The flame was made slightly "lean" in gas. The electrodes of the auxiliary spark were about 7 mm. apart.

Optical Arrangement.—A Bausch and Lomb quartz prism spectrograph was employed which has a dispersion of about 10 Å. per millimeter at λ2800. The center of the spark was focused on the slit by means of a cylindric quartz lens, which was found to give a fairly uniform distribution of intensity over the entire slit.

Sensitivity and Excitation.—The excitation obtained under the conditions described above approximates what should be expected in a very high temperature flame. Lines of very high excitation potential which do appear in the spark are not obtained, but, on the other hand, many lines appear, especially at high concentrations, which are so weak in flames that they are not photographed under ordinary conditions. For example, Mg λ2795, Mg λ2802, and B λ2479 appear strongly, and fourteen lines of Na, Mg, Zn, Au, Cd and Tl have been identified which did not appear in the flame in comparison experiments and are absent in the acetylene flame spectrograms of Lundegårdh.[2] The water and cyanogen bonds, of course, occur in the spectra obtained but on the whole the plates are cleaner and freer of background than those printed by Lundegårdh.

Photometry.—Since the purpose of the work outlined was to compare quantitatively the intensities of pairs of lines in the spark under various conditions, it was necessary to develop a method of rapid photometry. The intensities of two light sources are ordinarily compared photographically by cutting down one or both in a known way until the images which they produce on the photographic plate have the same density. This is most conveniently done by the use of rotating sectors, which are easily constructed and require no calibration. Calibration of wedges over a range of wave lengths is very laborious and screens could not be used in the present work.

The rotating sector has been condemned by some authorities because two effects, the "failure of the reciprocity law" and the "intermittency effect" may introduce large errors, but under certain conditions of operation these are found to counteract each other to a large extent,[3] and within sufficient accuracy the intensities of two lines of the same density are inversely proportional to the sector opening. It is necessary that the sector speed be maintained above a certain minimum (120 r. p. m. is sufficient), that the plates used are not too "slow," and that the total exposure time be kept constant. For an intermittent source such as the electric spark, the time of a single opening of the sector should be large in comparison to the duration of the flash, and to the time between flashes.

A step sector wheel was constructed similar to that shown in Fig. 3 except that it had three times as many steps with the same total range of opening. Each opening is the cube root of two times the one below it, corresponding to a 26% increase of exposure, except for a correction which had to be made due to the fact that the cylindrical lens did not give a quite

[3] (a) Weinland, *J. Optical Soc. Am.*, **15**, 337 (1927); (b) Weinland, *ibid.*, **16**, 295 (1928); (c) Weber, *Ann. Physik*, **45**, 801 (1914); (d) Howe, *Phys. Rev.*, **8**, 674 (1916); (e) Newcomer, *Science*, **49**, 241 (1919); (f) Rossler, *Ber.*, **59**, 2606 (1926); (g) Gibson and co-workers, Scientific Papers of the Bureau of Standards, No. 440 (1922).

uniform illumination over the entire slit. This sector was mounted as close as possible in front of the spectrograph slit and rotated at about 120 r. p. m. Every image of a spectral line of the plate then consists of a series of sections one above the other, of which the effective exposure increases logarithmically from the bottom to the top of the line.

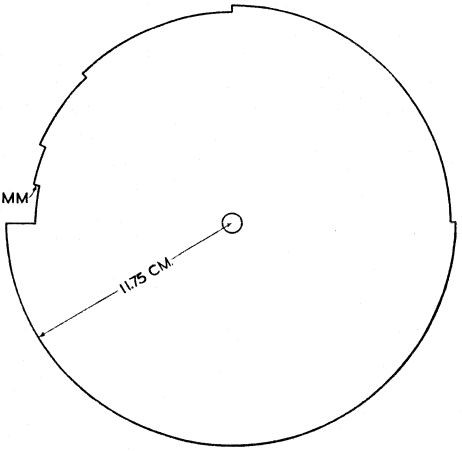


Fig. 3.—Rotating sector wheel used with photoelectric photometer.

If for a given spectral line the densities of the "sections" are plotted against the logarithms of the corresponding sector openings, a curve results whose shape depends on the characteristics of the plate and the development. Two spectral lines, sufficiently close so that the sensitivity and contrast of the plate are the same for both, will give curves of similar shape, but one will be displaced horizontally with respect to the other by an amount equal to the logarithm of the ratio of the intensities of the two lines in the source (see Fig. 4).

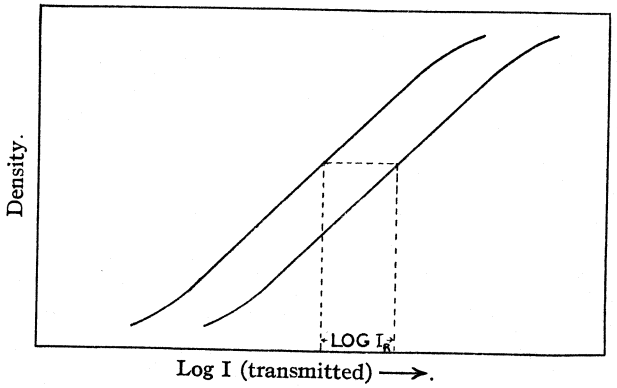


Fig. 4.—Typical intensity–photographic plate density curves for two sources of different intensities.

In practice, however, what one measures is an intensity due partly to the line emission of an element and partly to a continuous background which overlies the whole spectrum, and a correction must usually be made for the latter. It was found that where a sufficiently wide slit was used to permit of photometering the lines with an ordinary photoelectric photom-

eter, the blackening due to the background was such a large part of the total that the errors of measurement were very large.

However, it was found that the spectrograph slit could be narrowed sufficiently to make the density of the background negligible in comparison to that of the spectral lines, leaving the lines still sufficiently wide to be compared visually. When two lines were to be compared the photographic plate was cut between them, and the two portions brought into contact so that the two lines were side by side. One portion of plate was then moved up and down until opposite to one section of one line a section of the other line of equal density was found. If no exact correspondence could be found an interpolation was made. Knowing the sector openings corresponding to the sections chosen the relative intensities of the lines were easily estimated.

Two types of plates were used: Eastman D. C. Ortho with the ordinary Eastman D 61a developer, and Eastman "Regular" lantern slide plates with the contrast developer recommended. The former plates were developed for four minutes, the latter for two, stroking with a camel's hair brush, which gives exceptionally even development.

Experimental Results and Discussion

In order to make an estimate of the accuracy which might be expected of the analysis of simple solutions using the methods outlined, some intensity–concentration curves were first determined, as shown in Fig. 5. In each case the lines of the elements studied were compared with the copper line λ3247, which was photographed by making each test solution 0.01 molal in copper nitrate. These curves should not be compared too rigorously with one another, since the plate sensitivity and contrast varies somewhat over the spectral region included.

The mutual effects which various elements have on each other's excitation were then studied. Since, as mentioned above, the atomizing of reasonable amounts of substances into a suitable flame did not appreciably change its temperature or volume, two principal effects remain to be considered. The introduction of substances of low ionization potential into the flame may be expected to change the conductivity and consequently the nature of the discharge and the excitation of all other elements present. Secondly, elements of low resonance potential when added may rob other elements of high excitation potential of their energy in collisions of the second kind, and cause their emission to be diminished.

A standard solution was prepared, 0.01 molal in copper, 0.01 molal in silver, 0.1 molal in thallium and 0.1 molal in cadmium, and the spark-in-flame spectrum of this was photographed beside the spectrum of another solution which was identical except for the addition of a rather large amount (1 molal) of a fifth element. In successive experiments this added element

TABLE II

Line	Exc. v.	Percentage change in intensity due to presence of 1 molal — Sodium				Av.	Copper				Av.	Silver				Av.	Mercury		Av.	Percentage error in analysis due to Na	Cu	Ag	Hg
3247 Cu	3.8	+26	+12	+26	+26	+23						+10	+10	+5	+5	+6	0	0	0	+25	..	+6	0
3274 Cu	3.8	+17	+12	+20	+28	+19						+7	+7	0	−5	+2	0	0	0	+20	..	+2	0
3281 Ag	3.7	+ 6	+ 4	+11	+14	+ 9	0	0	− 2	−2	−1						+5	0	+3	+18	− 2	..	+ 6
3384 Ag	3.6	0	0	+ 7	+ 9	+ 4	−3	−2	− 3	−2	−3						+5	0	+3	+20	−15	..	+15
3775 Tl	3.27	+34	+26	+26	+26	+28	−3	0	+11	+3	+3	− 3	− 3	0	0	−2	0	0	0	+60	+ 6	− 4	0
3519 Tl	4.3	+51	+41	+68	+58	+54	−3	0	0	0	−1	+12	+12	0	0	+6	−5	−5	−5	+90	− 2	+10	− 9
3261 Cd[a]	3.78	Decrease					Small decrease					0	0	0	0	0	0	0	0				
3610 Cd[a]	7.5	Decrease					Small decrease					0	0	0	0	0	0	0	0				
3460 Cd[a]	7.5	Decrease					Small decrease					0	0	0	0	0	0	0	0				
Resonance energy of element added (volts)																				2.1	3.8	3.6	4.9

[a] Cadmium lines were too weak to estimate accurately, but intensity change was small (less than 20%).

was varied, elements being chosen with widely different resonance and ionization potentials. The percentage changes in the intensities of certain copper, silver and thallium lines due to the addition of the "impurity" are given in Table II. The four determinations indicate the accuracy of the intensity comparisons.

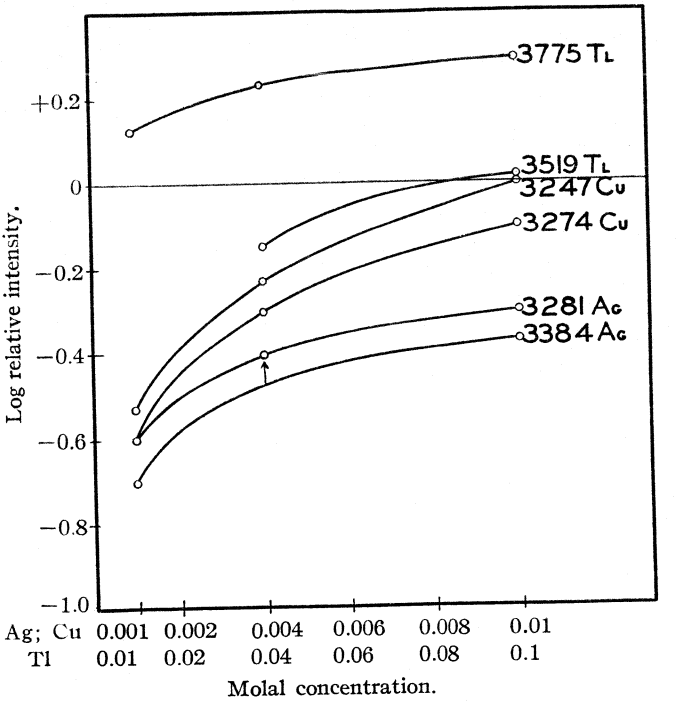


Fig. 5.—Intensity–concentration curves for several elements.

It will be noticed that the line intensities are usually increased by the "impurity" probably due to the increased conductivity of the flame gases. The last four columns of the table show the per cent. errors which these changes in intensity would cause in an analysis for copper, silver and thallium in case unknown solutions of approximately the same composition as those of the four solutions containing the "impurities" were compared directly with a test solution containing the three elements in the same concentration, but without the impurity. It will be seen that these errors are not larger than the average error of estimation except in the case of sodium.

Conclusion

One of the principal objects of the present work was to find conditions under which the spectroscopic analysis of solutions containing several elements in rather widely varying relative concentrations can be made rapidly

without elaborate calibration experiments being necessary for each special case. Since under the conditions of the spark-in-flame the mutual effects of elements are in general not large, it appears that such analyses can be carried out with moderate precision if the intensities of the lines emitted by the unknown solutions are compared directly with the concentration intensity curves which have been determined once and for all on pure test solutions of the elements in which one is interested. In case alkali metals are present in high concentration their effect can be to a considerable extent allowed for by the addition, in known concentration, of a reference element absent in the unknown. This is the method of "Leitlinien" discussed by Lundegårdh.[2]

Summary

1. A new method of exciting spectra for the purpose of quantitative chemical analysis has been developed and studied. It consists in passing a condensed spark discharge through a flame into which is atomized a solution of the sample to be analyzed.

2. The excitation obtained, though less than that of the ordinary spark, is similar to that which should be expected in a flame of very high temperature, and many lines appear which are absent in ordinary flame spectra.

3. The mutual effects of some elements on each other's emission in the spark-in-flame have been studied, and these have been found small enough to permit of a semi-quantitative analysis of unknown solutions containing several elements, without elaborate calibration experiments.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

ACTION OF RADON ON SOME UNSATURATED HYDROCARBONS. II. PROPYLENE AND CYCLOPROPANE

BY G. B. HEISIG

RECEIVED FEBRUARY 15, 1932 PUBLISHED JUNE 6, 1932

In a previous paper[1] the action of radon on five unsaturated hydrocarbons was reported. It was shown that the number of molecules condensed per ion pair formed ($-M/N$) was additive and constitutive. A method of calculating the values of $-M/N$ was devised for these hydrocarbons based on the values for ethylene and acetylene whose polymerizations had been studied previously by Lind and Bardwell.[2] Moreover, the writer[3] has shown that the relation between the heats of formation and the $-M/N$ values may be used as a basis for predicting the approximate values of the $-M/N$.

In order to compare these two methods of predicting the $-M/N$ and to obtain further knowledge of the condensations produced by radon so that

[1] Heisig, THIS JOURNAL, **53**, 3245–3263 (1931).

[2] Lind and Bardwell, *ibid.*, **48**, 1559, 1564 (1926).

[3] Heisig, *J. Phys. Chem.*, **36**, 1000–1005 (1932).

the mechanism of the condensation process may be further clarified, the polymerization of the isomers propylene and cyclopropane was investigated.

The procedure and the methods of calculation were those used in the previous paper.[1] The results of this present work may be summarized as follows.

TABLE I

SUMMARY OF RESULTS

	P. drop of HC., mm.	% of P, drop used in calcn. of $-M/N$	$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta HC.}$	$-M/N$ Product	
Propylene	501.2	96.2	14.4	4.9	Colorless mobile liquids
Cyclopropane	411.9	100.0	20.5	3.3	

The method for calculating the $-M/N$ in the first paper was to neglect the hydrogen atoms involved and assign 2 for a methyl group, and 4.8 to a double bond. A substituent entering a terminal unsaturated carbon atom reduces the sum of the values by 50%. The calculated $-M/N$ of propylene is $(4.8 + 2)/2 = 3.4$. This is to be compared with an experimental value of 4.9. Cyclopropane acts both as a saturated and as an unsaturated paraffin. For example, it reacts with chlorine to give substitution products. When treated with bromine, concentrated sulfuric acid, or a 2% potassium permanganate solution, it reacts to give derivatives of propane. However, the action is very much slower than the corresponding action with propylene. In lieu of other information, cyclopropane would be expected to have a $-M/N$ which would be intermediate between that of the saturated hydrocarbon propane and that of the corresponding double bonded derivative, propylene. The $-M/N$ for propane is practically 2 and that for propylene is 4.9, which gives an average 3.5.

The $-M/N$ values increase with the increase of the negative heat of formation from atoms in their standard states, and the value for compounds with positive heats of formation is about 2. The heat of formation of ethylene is -6.1 kg.-cal. and the $-M/N$ is 4.8. Since the heat of formation of propylene is -2 kg.-cal., the $-M/N$ for propylene would be expected to be about 4.8 and this value agrees with that obtained by experiment. The change in the $-M/N$ with heat of formation is small. The $-M/N$ for allylene is 8.3 and the heat of formation is -45.2 kg.-cal.

The values of the $-M/N$ were shown[1] to be larger the smaller the value of $\Delta(H_2 + CH_4)/-\Delta HC.$ for the two and four carbon derivatives which had been studied. It was further shown that the order of the increase in the $-M/N$ was: the saturated hydrocarbon, the ethylene derivative and the acetylene derivative. That the same relation holds for the propane derivatives is shown in Table II.

The position of cyclopropane between that of propane and propylene with respect to the $\Delta(H_2 + CH_4)/-\Delta HC.$ is in agreement with its chemical properties.

TABLE II

RELATION OF $-M/N$ AND EVOLUTION OF $H_2 + CH_4$ TO UNSATURATION

	$\frac{\Delta(H_2 + CH_4)100}{-\Delta HC.}$	$-M/N$
Propane	82.3	1.7
Cyclopropane	20.5	3.3
Propylene	14.4	4.9
Propine	6.1	8.3
Allene ($H_2C{=}C{=}CH_2$)	4.9	10.4

The condensation products which were obtained from these two hydrocarbons were light mobile oils with similar characteristics. The increase in the $\Delta(H_2 + CH_4)/-\Delta HC.$ as the action progressed indicated that the products lost hydrogen and methane because of their bombardment by the alpha-particles. A quantity of the condensation product of propylene is being prepared with the idea of obtaining some of its physical and chemical properties as well as its average molecular weight. From the molecular weight it is hoped to obtain some idea as to the average number of alpha-particles involved in the formation of the average molecule.

Experimental

Propylene

Purification.—Propylene[4] having a purity of 99.5% was dried by passing through phosphorus pentoxide, and purified by four low temperature distillations. The vapor pressure of the sample at the temperature of solid carbon dioxide agreed with that given by Burrell and Robertson.[5]

Action with Radon.—Very shortly after mixing the propylene with radon a fog appeared. The product collected as a mobile colorless oil on the bottom of the reaction vessel. The ratio $\Delta(H_2 + CH_4)/-\Delta HC.$ increased from about 10% to about 25% as the action progressed. The results are given in Table III. When these data are plotted, the logarithm of the total pressure against the percentage of radon gives a somewhat concave curve while the plot of the logarithm of the pressure of the hydrocarbon against the per cent. of radon is a straight line. The pressure of the hydrogen and methane evolved when plotted against the percentage of radon gives a slightly convex curve.

Cyclopropane

Purification.—Cyclopropane[4] having a purity of 99% was bubbled slowly—one bubble a second—through a 1% solution of potassium permanganate and then through 50% potassium hydroxide. The gas after being dried by passing through a trap maintained at $-30°$, a calcium chloride tube and finally through a tube of phosphorus pentoxide was condensed in a trap immersed in liquid air. It was then further purified by low temperature distillations until the vapor pressure was constant at the temperature of solid carbon dioxide after five distillations. The purity of the sample was further proved by determining the molecular weight using the method and apparatus of Maass and Russell.[6] A molecular weight of 41.93 was obtained under ideal conditions.

[4] Obtained from the Ohio Chemical Co., Cleveland, Ohio.

[5] Burrell and Robertson, "Vapor Pressures of Various Compounds at Low Temperatures," Tech. Paper 142, Bureau of Mines.

[6] Maass and Russell, THIS JOURNAL, **40**, 1847–1852 (1918).

TABLE III

POLYMERIZATION OF PROPYLENE BY ALPHA RAYS FROM RADON

xC_3H_6 gas $\longrightarrow$ $(C_3H_6)_x$ liq. Temp. 25°; $is = 2.58$; $i = 1.25$; $s = 2.09$; Reaction Sphere: vol., 28.250 cc.; radius, 1.889; E, 0.04638 curie.

Time Days	Time Hours	Radon %	Total	Pressure of C_3H_6	$H_2 + CH_4$	$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta HC.}$	Velocity constant $(k\mu/\lambda)'$	$\frac{-M_{C_3H_6}}{N_{C_3H_6^+}}$
		100.00	675.8	675.8				
	2.00	98.511	661.5	660.5	1.0	6.7	33.0	4.9
	5.33	96.079	639.3	635.9	3.4	9.8	33.7	4.9
	10.57	92.279	607.2	600.6	6.6	9.1	32.4	4.7
	15.62	88.946	593.3	569.5	9.8	10.3	34.4	5.1
1	3.10	81.608	525.1	508.6	16.5	11.0	33.2	4.9
1	7.10	79.196	508.8	490.6	18.2	9.4	32.2	4.9
1	11.13	76.838	494.3	473.4	20.9	15.7	32.6	4.9
1	16.32	73.905	476.6	453.0	23.6	13.2	32.3	4.9
2	3.00	68.215	444.7	416.7	28.0	12.1	31.7	4.9
2	7.20	66.103	434.9	404.2	30.7	21.6	31.1	4.9
2	12.42	63.563	422.5	389.5	33.0	15.6	31.5	4.9
3	2.85	57.041	393.6	355.5	38.1	15.1	30.2	4.9
3	12.03	53.249	378.1	337.3	40.8	14.8	29.9	4.7
4	3.95	47.610	357.5	312.0	45.5	18.6	29.8	4.7
4	12.43	44.344	346.2	298.7	47.5	14.0	29.1	4.7
5	3.80	39.513	330.8	279.3	51.5	20.6	29.9	4.9
5	12.35	37.062	324.0	271.4	52.6	14.0	25.3	4.2
6	2.87	33.232	313.4	257.5	55.9	23.8	29.6	4.9
6	12.5	30.922	307.8	250.2	57.6	23.3	26.9	4.3
7	2.83	27.772	299.6	239.6	60.0	22.7	29.6	4.9
7	11.97	25.918	295.0	233.8	61.2	20.7	28.7	4.9
8	4.13	22.971	288.7	227.0	61.7	7.4	21.6	3.6
9	5.32	19.018	279.8	215.1	64.7	25.2	29.4	4.7
10	11.37	15.181	269.4	201.6	67.8	22.9	36.4	5.7
11	12.22	12.599	263.1	193.8	69.3	19.3	32.2	5.3
12	11.90	10.548	259.8	189.3	70.5	26.7	39.2	6.2
17	5.77	4.492	249.1	174.6	74.5	27.2	28.9	4.5
					Weighted average	14.4		4.9

Action with Radon.—Within five minutes after mixing the cyclopropane with radon, a dense fog appeared. After six hours a small pool of a mobile colorless liquid condensate had formed in the reaction sphere. The results are given in Table IV. The graphical representation is quite similar to that of propylene.

TABLE IV

POLYMERIZATION OF CYCLOPROPANE BY ALPHA RAYS FROM RADON

xC_3H_6 $\longrightarrow$ $(C_3H_6)_x$ liq. Temp., 25°; $is = 2.58$; $i = 1.25$; $s = 2.09$; Reaction Sphere: vol., 29.850; radius, 1.924; E, 0.04806 curie.

Time Days	Time Hours	Radon %	Total	Pressure of C_3H_6	$H_2 + CH_4$	$\frac{\Delta(H_2 + CH_4)}{-\Delta HC.}$	Velocity constant $(k\mu/\lambda)'$	$\frac{-M_{C_3H_6}}{N_{C_3H_6^+}}$
		100.00	683.5	683.5				
	1.5	98.882	675.5	675.0	0.5	5.9	23.1	3.5
	6.03	95.579	652.3	650.2	2.1	6.5	23.5	3.6
	10.5	92.427	633.1	628.7	4.4	10.7	22.3	3.4

TABLE IV (*Concluded*)

Time Days	Time Hours	Radon %	Total	Pressure of C_3H_6	$H_2 + CH_4$	$\frac{\Delta(H_2 + CH_4)}{-\Delta HC.}$	Velocity constant $(k\mu/\lambda)'$	$\frac{-M_{C_3H_6}}{N_{C_3H_6^+}}$
	14.55	89.662	617.8	610.7	7.1	15.0	22.7	3.4
	18.0	87.372	605.5	595.7	9.8	18.0	21.5	3.3
	22.45	84.531	589.3	577.2	12.1	12.4	23.1	3.5
1	8.67	78.271	559.8	542.3	17.5	15.5	20.7	3.2
1	12.55	76.025	549.7	529.7	20.0	19.9	21.8	3.3
1	16.97	73.544	538.8	516.6	22.2	16.8	20.9	3.2
1	21.87	70.891	527.1	502.3	24.8	18.2	22.0	3.4
2	8.78	65.324	502.1	471.5	30.6	18.5	23.7	3.7
2	17.87	61.017	488.2	454.6	33.6	17.8	17.8	2.8
2	21.4	59.424	482.3	446.0	36.3	31.4	25.0	3.9
3	8.68	54.600	465.9	425.6	40.3	19.6	20.2	3.2
3	13.77	52.560	460.0	417.6	42.4	26.2	19.3	3.1
3	21.0	49.783	451.6	406.5	45.1	24.6	20.2	3.2
4	8.65	45.619	439.4	390.3	49.1	24.7	20.4	3.3
4	22.22	41.214	427.1	374.3	52.8	25.4	19.9	3.2
5	10.71	37.522	418.0	361.8	56.2	27.2	19.1	3.1
5	21.4	34.632	411.3	351.8	59.5	33.0	20.2	3.3
6	8.67	31.824	404.1	342.2	61.9	25.0	20.5	3.2
8	14.5	21.254	382.4	312.2	70.2	27.7	18.1	3.0
11	15.53	12.290	366.0	288.3	77.7	31.4	18.5	3.1
15	20.5	5.767	355.7	271.6	84.1	38.4	19.0	3.1
						Weighted average 20.5		3.3

Summary

The action of radon on propylene and cyclopropane has been studied and the $-M/N$ ratios have been found to be 4.9 and 3.3, respectively.

The $-M/N$ values calculated by two methods have been compared with the experimental values.

The associations of lower values of $\Delta(H_2 + CH_4)/-\Delta HC.$ with higher $-M/N$ values is again observed

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ALDEHYDE BISULFITE COMPOUNDS. I. THE RATE OF DISSOCIATION OF BENZALDEHYDE SODIUM BISULFITE AS MEASURED BY ITS FIRST ORDER REACTION WITH IODINE

BY T. D. STEWART AND L. H. DONNALLY

RECEIVED FEBRUARY 23, 1932 PUBLISHED JUNE 6, 1932

An excellent résumé of the work done prior to 1926 on aldehyde and ketone bisulfites is given by Raschig and Prahl,[1] who also give evidence that in the aldehyde bisulfite ion the sulfur is attached directly to the carbon, as in a sulfonic acid. They leave open, however, the question of why these compounds, as contrasted with most sulfonic acids, are very easily decomposed both in acid and alkaline solution. In spite of the enormous amount of work that has been done upon compounds of this type,[2] the questions of structure and of mechanism of formation and dissociation may be considered unsettled. For this reason a very detailed study has been undertaken.

The reaction of benzaldehyde with sodium bisulfite to form an addition product is reversible, with the equilibrium favoring the addition product.

$$C_6H_5C(H)=O + Na^+ + HSO_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5C(H)(OH)SO_3^- + Na^+ \qquad (1)$$

This system is oxidized by iodine to form benzaldehyde and sulfate ion.

$$C_6H_5C(H)(OH)SO_3^- + H_2O + I_3^- = C_6H_5C(H)=O + SO_4^= + 3H^+ + 3I^- \qquad (2$$

The first step in this work was to show that the rate of the reaction (2) was independent of the concentration of iodine.

Experiment.—500 cc. of benzaldehyde bisulfite solution equivalent to 51 cc. of 0.1 *N* iodine was put into each of two flasks. In one flask 36 cc. of iodine was added at one time; the iodine was decolorized in 378 minutes. In the other flask 36 cc. was added in 2 to 3 cc. portions, additions being made immediately after the iodine color faded. The 36 cc. of iodine was used up in 379 minutes. The approximate hydrogen-ion concentration in these two experiments was 0.01 *N*. In Fig. 1 the plot of the logarithm of the concentration of the unreacted benzaldehyde bisulfite against time is a straight line, for the second experiment. It will be seen later that small changes in the hydrogen-ion concentration during this experiment were unimportant.

Effect of Hydrogen Ion upon the Rate of the Reaction.—In buffered solutions it was necessary to measure the change in hydrogen-ion concentration as the reaction proceeded because of the sensitiveness of the reaction rate to change in acidity at low acid concentrations, and because of the acid produced by the reaction. The hydrogen-ion

[1] Raschig and Prahl, *Ann.*, **448**, 265–312 (1926).

[2] See Kerp, "Schweflige Säure und ihre Verbindungen mit Aldehyden und Ketonen," Verlag von J. Springer, Berlin, 1904; Schroeter, *Ber.*, **61**, 1616 (1928); C. Wagner, *Ber.*, **62**, 2873 (1929).

concentrations were measured by means of a glass electrode, using a potentiometer and galvanometer, to an accuracy of 0.02 P_H.[3] In order to illustrate the method of obtaining the specific reaction rate at a specified value of P_H the runs made in the region of P_H 6.2 to 6.9 will be described in detail.

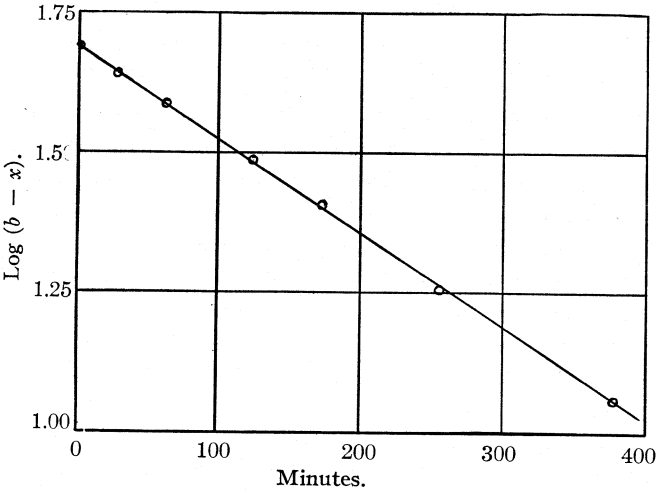


Fig. 1.—The reaction rate of sodium benzaldehyde bisulfite with iodine at about P_H 2.

Experiment.—A stock of buffer solution was made from phosphoric acid and sodium hydroxide (total phosphate, 0.111*M*), to give a P_H within the range desired, as measured by the electrode. To 500 cc. of the buffer solution was added 4.0 cc. of a sodium benzaldehyde bisulfite solution which was equivalent to about 100 cc. of 0.1 *N* iodine, to make the reaction mixture. All solutions were prepared from water boiled to remove oxygen, and were stored in nitrogen. Portions of this reaction mixture were brought to the temperature of the thermostat and 10.00-cc. portions of the standard iodine solution, which was at the same temperature, added. The time for decolorization of the iodine was noted and another portion of iodine added immediately. The data for a typical experiment are given in Table I and plotted in Fig. 2.

TABLE I

THE SPECIFIC REACTION RATE IN PHOSPHATE BUFFER AT P_H 6.46 TO 6.72

x, amount of iodine used; *b*, total amount of benzaldehyde bisulfite present expressed in cc. of iodine. Temp., 0°C. ±0.5°

x	*b* − *x*	log 1/*b* − *x*	Seconds
0.00	90.36	−1.956	0
25.00	65.36	−1.815	5
50.00	40.36	−1.606	15
70.00	20.36	−1.309	32
85.00	5.36	−0.729	74

The points do not lie on a straight line (compare Fig. 1), apparently because of changing hydrogen-ion concentration. This assumption is made because doubling the concentration of the buffer and thereby in-

[3] Robertson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 5 (1931).

creasing the ionic strength gave practically the same specific rate of reaction and decreased the above-mentioned curvature. Also the percentage changes in hydrogen-ion concentration and in specific reaction rate during the reaction were of the same order of magnitude, each about 100%. The specific reaction rates at selected points were therefore obtained by drawing tangents to this curve (Fig. 2). The P_H of the solution at these same points was obtained as follows.

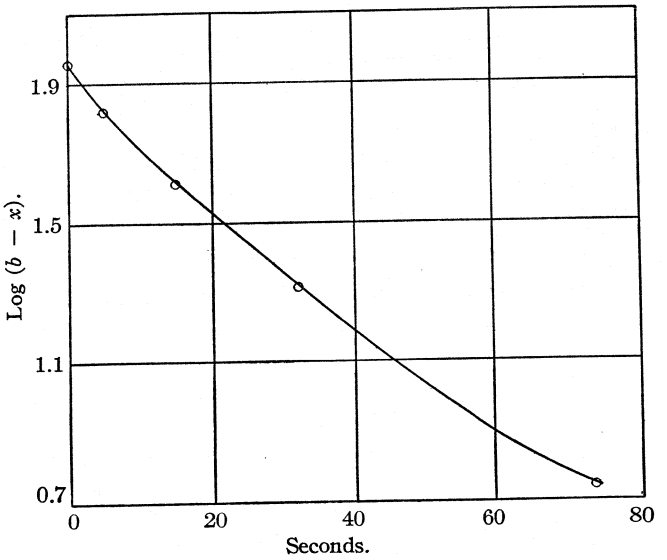


Fig. 2.—The reaction rate in the P_H range 6.45 to 6.72.

A similar portion of the reaction mixture was taken and the iodine added as before. After each decolorization the electrode reading was taken. These readings were plotted against the corresponding calculated P_H value using Sörensen's phosphate buffer solutions of P_H 6.24, 6.81 and 7.38 to calibrate the electrode. The electrode was calibrated both before and after each experiment and shown to be reliable. From this plot (not given), the P_H value of the reaction mixture could be read for any selected time during the reaction. The results of the experiments and calculations in the phosphate buffer range are presented in Table II.

TABLE II

THE SPECIFIC REACTION RATE FOR THE PHOSPHATE P_H RANGE AT VARIOUS TEMPERATURES, IN EQUIVALENTS PER SECOND

0.0° k_1 (sec.)	P_H	5.5° k_1 (sec.)	P_H	9.5° k_1 (sec.)	P_H	21.0° k_1 (sec.)	P_H
0.0535	6.72	0.0875	6.72				
.0482	6.66	.0730	6.60				
.0437	6.60	.0596	6.50	.109	6.60		
.0316	6.46	.0538	6.46	.0945	6.50	0.372	6.50

Similar measurements for the P_H range 3.6 to 5.6 were made in exactly the same manner as in the range 6.24 to 7.38. Acetic acid–sodium acetate buffers of Walpole-Clark were used as standards. The stock buffer solution was made with a total acetate concentration of 0.111 M and 500 cc. was used as before for the preparation of the reaction mixture. Table III contains the results of the experiments and calculations in this range.

TABLE III

THE SPECIFIC REACTION RATE FOR THE ACETIC–ACETATE BUFFER RANGE, IN EQUIVALENTS PER SECOND

9.5°		21°	
k_1 (sec.)	P_H	k_1 (sec.)	P_H
0.00292	4.91		
.00276	4.88	0.01015	4.88
.00251	4.84	.00923	4.86
.00218	4.78	.00822	4.78
.00195	4.74	.00785	4.76

Determinations were also made with chloroacetic acid–chloroacetate and phosphoric acid–monosodium phosphate buffers. Both buffer solutions were made up with the total anion concentration 0.111 M and in each of these the hydrogen-ion concentration was measured by a hydrogen electrode. The results are given in Table IV. In Table IV are also results obtained by using measured concentrations of hydrochloric acid.

TABLE IV

THE SPECIFIC REACTION RATE AT HIGHER ACID CONCENTRATIONS, AT VARIOUS TEMPERATURES, IN EQUIVALENTS PER MINUTE

Part A. Chloroacetate Buffer Range			Part B. Acid Phosphate Buffer Range		
Temp., °C.	k_1 (min.)	P_H	Temp., °C.	k_1 (min.)	P_H
20.95	0.01007	3.00	20.84	0.00392	2.30
31.58	.0335	3.00	31.77	.0146	2.30
20.99	.00923	2.96	20.90	.00378	2.27
31.59	.0307	2.96	31.78	.0140	2.27
21.06	.00849	2.92	20.92	.00364	2.23
31.59	.0282	2.92	31.81	.0137	2.23
Part B. Acid Phosphate Buffer Range			Part C. Hydrogen Chloride Solution		
20.90	0.00324	1.90	19.8	0.00450	1.00
31.74	.0122	1.90	29.0	.0154	1.00
20.90	.00313	1.85	19.8	.00904	0.55
31.78	.0120	1.85	29.1	.0317	.55
			20.5	.0286	.03
			28.8	.0903	.03

Calculations of the rates for different hydrogen-ion concentrations were made by interpolation for the single temperature of 21°. These are presented in Table V and plotted in Fig. 3.

TABLE V

SUMMARY OF DATA, CALCULATED FOR 21°, ON EFFECT OF CHANGING HYDROGEN-ION CONCENTRATION UPON THE SPECIFIC REACTION RATE (PLOTTED IN FIG. 3) AND UPON THE APPARENT HEAT OF ACTIVATION (FIG. 4)

P_H	k_1 (min.)	Q (calcd.)	P_H	k_1 (min.)	Q (calcd.)
6.50	22.3	18,900 ± 1,000	2.23	0.00377	21,700 ± 300
4.86	0.554	19,100 ± 500	1.90	.00328	22,000 ± 300
3.00	.0101	20,100 ± 300	1.85	.00322	22,100 ± 300
2.97	.00923	20,200 ± 300	1.00	.00529	23,300 ± 300
2.92	.00849	.....	0.55	.0106	23,800 ± 300
2.30	.00405	21,300 ± 300	.03	.0307	24,100 ± 300

Variation of Specific Reaction Rate with Temperature and the Apparent Heat of Activation.—Practically every determination of the specific reaction rate was made at two or more temperatures. Data for the neutral phosphate range are given in Table II, those for the acetic–acetate range in Table III, those for chloroacetic–chloroacetate, acid phosphate and all others are summarized in Table IV.

The data in Tables II and III were used as follows. The P_H values were plotted against log k_1 for each temperature, and a straight line of unit slope was drawn through the points. This was justified in this range of P_H by the rate of change of reaction rate with change in P_H as given in Fig. 3. In those cases where the accuracy was high the points fell well on the line. From each of these curves at an arbitrary P_H a value of k_1 was taken and in turn plotted against the corresponding value of $1/T$. From the slope of the best straight line was calculated (Table V) the apparent heat of activation, using the equation $Q/R = -\mathrm{d} \ln k_1/\mathrm{d}(1/T)$. The change in heat of activation with change in P_H is plotted in Fig. 4.

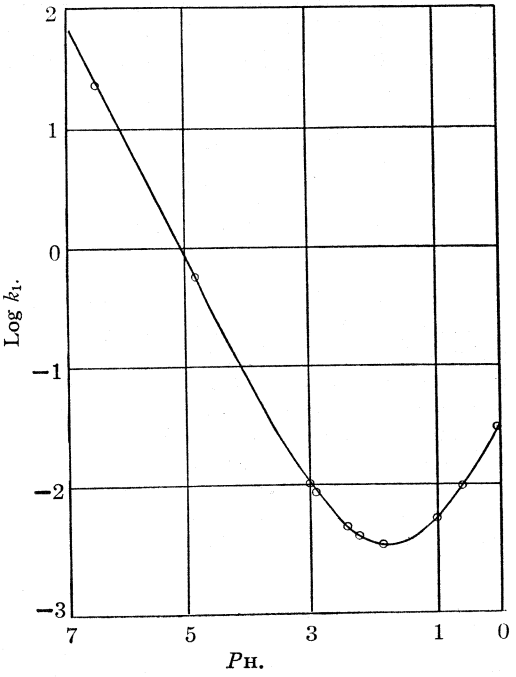


Fig. 3.—The change in the reaction rate with changing P_H.

Identity of the Iodine Reaction with the Dissociation Reaction.—Since the rate of reaction (2) is independent of the concentration of iodine, there is little doubt that the rate thus measured is the rate of the reverse step

of reaction (1). In order to test this point, the rate of attainment of equilibrium of (1) was measured.

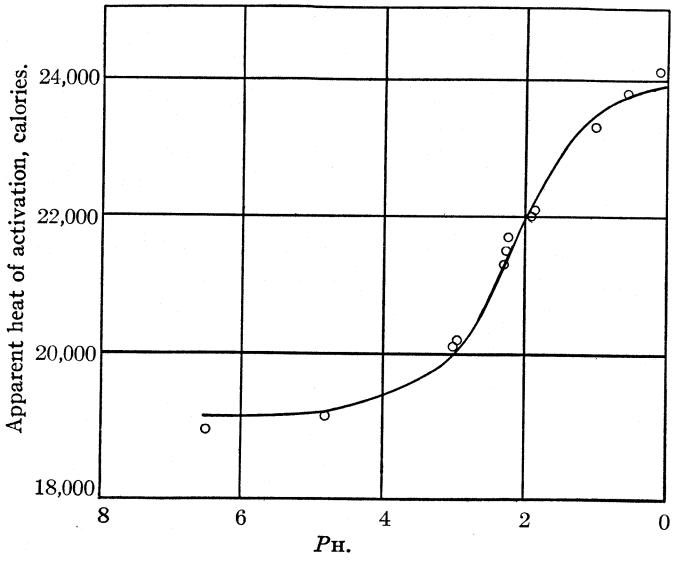


Fig. 4.—Change in the apparent heat of activation with change in P_H.

Experiment.—To 1 liter of 0.25 *N* hydrochloric acid was added an amount of 0.8 *M* sodium benzaldehyde bisulfite equivalent to 0.239 liter of 0.1180 *M* iodine solution; 0.029 liter of the iodine solution was added and the time when the solution became colorless was recorded as zero time. The solution was then allowed to stand for a specified time for dissociation to take place and then iodine in slight excess of the amount of bisulfite ion formed was added and the excess back titrated. The time that iodine was present in the solution was measured to give a correction for the amount of iodine used simultaneously according to equation (2). Sodium bicarbonate was then added and the amount of total unused benzaldehyde bisulfite determined by titration. The data obtained are given in Table VI.

TABLE VI

COMPARISON OF THE IODINE AND DISSOCIATION REACTIONS

cc_1 is the amount of bisulfite ion (in cc. of 0.1180 *N* iodine) produced after time t_1 in the absence of iodine; cc_2 the volume of iodine used up in elapsed time t_2 in the continued presence of iodine; cc_3 the reaction rate calculated by Equation 5 (Fig. 5)

cc_1	t_1	cc_2	t_2	cc_3	t_3
8.30	5.50	5.00	3.4	5.0	3.24
15.15	10.1	10.0	6.78	10.0	6.55
24.30	20.31	20.0	15.6	20.0	13.42
31.07	29.4	25.0	21.2	30.0	20.70
36.90	45.2	27.0	23.7		
39.0	60.3	30	28.7		
41.0		35	40.0		
		38	52.0		

The limiting amount of bisulfite produced in this experiment was taken to be the equilibrium amount and the equilibrium constant was calculated thereby. Experiments were also made to determine the rate of the reaction in the constant presence of iodine for the same solution and the data are given in the third and fourth columns of Table VI. From the rate of the reaction in the continued presence of iodine ($k_1 = 0.00755$) and the

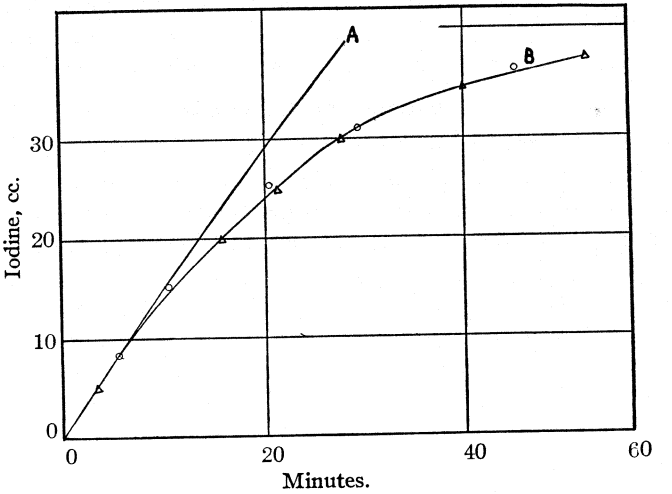


Fig. 5.—Comparison of reaction rate in the presence of (Curve A) and absence of iodine (Curve B); the approach to equilibrium (Δ, calculated; O, experimental, Curve B).

equilibrium constant ($K_E = 0.98 \times 10^3$) the forward rate (k_2) was calculated as equal to 7.4 for P_H of about 1.6. The concentration and time units for these figures are moles per liter and minutes, respectively. The equation expressing the velocity of the net change after t minutes for this bimolecular reaction opposing the monomolecular is

$$\frac{dx}{dt} = k_1(b - x) - k_2x(a + x) \qquad (4)$$

where b and a are, respectively, the initial concentrations of addition product and of benzaldehyde.

Integrated, this gives

$$t = \frac{2.3}{k_2\sqrt{\left(\frac{k_1 + k_2a}{k_2}\right)^2 + \frac{4k_1b}{k_2}}} \log \frac{\frac{k_1 + k_2a}{2k_2} + {}^1/_2\sqrt{\left(\frac{k_1 + k_2a}{k_2}\right)^2 + \frac{4k_1b}{k_2}} + x}{\frac{k_1 + k_2a}{2k_2} - {}^1/_2\sqrt{\left(\frac{k_1 + k_2a}{k_2}\right)^2 + \frac{4k_1b}{k_2}} + x} \qquad (5)$$

By substituting the above values in the equation we may calculate the data given in Table VI, columns one and two. These calculations are given in the last two columns of Table VI and together with points for the reaction in continual presence of iodine are plotted in Fig. 5.

The conclusion is drawn from these curves that the dissociation reaction in the absence of iodine has the same specific rate as the reaction in the presence of iodine, since in the limit, as the elapsed time becomes short, the rate of production of instantly titratable sulfite becomes the same in the presence and absence of iodine. The multiple ionizations of sulfurous acid and of the addition compound permit several paths for the reactions of addition and of dissociation but these ionizations are presumably maintained in equilibrium. Any extremely rapid isomerization could not be detected by these measurements. These factors will be discussed in a later paper.

Summary and Conclusion

1. Sodium benzaldehyde bisulfite reacts with iodine at a rate independent of its own concentration and of that of the iodine.

2. The rate determining step is the dissociation into bisulfite or sulfite ion. There is no evidence of the presence of isomers of the bisulfite compound.

3. The rate changes with changing hydrogen-ion concentration, being very rapid at low hydrogen-ion concentration reaches a minimum at P_H 1.8, and increases again with higher concentrations of acid.

4. The apparent heat of activation has been measured and found to vary with changing hydrogen-ion concentration.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 66]

THE ROLE OF LIQUID STATIONARY FILMS IN BATCH ABSORPTION OF GASES. III. RATES OF HYDROGEN ABSORPTION AND RELATIVE RATES OF CATALYTIC HYDROGENATION IN ALCOHOL[1]

BY HAROLD S. DAVIS,[2] GEORGE THOMSON[3] AND GEORGE S. CRANDALL[3]

RECEIVED MARCH 1, 1932 PUBLISHED JUNE 6, 1932

During hydrogenations in solutions with metallic catalysts, the reaction proper must take place at or close to the surface of the solid. There is also good evidence that the course by which the hydrogen reaches this

[1] This paper contains in part results obtained in an investigation on the "Relative Rates of Reaction of the Olefins" listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Research and Development Department, Vacuum Oil Company, Inc., Paulsboro, N. J.

[3] Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

position is somewhat as follows. The very surface of the liquid is always practically saturated with dissolved hydrogen; thence the dissolved gas penetrates to the interior of the liquid mainly by diffusion through an unstirred layer beneath the liquid surface (liquid stationary film), it is distributed uniformly through the main body of the liquid by currents and finally passes thence to the surface of the catalyst by diffusion through another unstirred layer of liquid existing at the solid–liquid interface.

The stationary films are by no means monomolecular in thickness, nor must they be confused with adsorbed layers. Even in highly agitated liquids, they are much thicker. Strong evidence for their existence can be cited from the studies of numerous investigators on the rates of solution of solids and gases by liquids. Additional evidence is found in the phenomena attending the transfer of heat between phases. In the present and in the two former papers in this series[4] it has been assumed that the limits of the stationary films are sharply defined. It is noteworthy that by this same approximation, "The convection loss from bodies of simple geometric form, under widely different fluid conditions, can be computed by means of a few convenient equations," ["International Critical Tables," Vol. V, 1929, p. 234].

The first part of the present investigation deals with a study of the rates of hydrogen absorption during hydrogenations of olefins in alcohol with platinum platinum-oxide catalyst.

The catalytic reduction apparatus[5] used was that designed by Professor Roger Adams and his associates. The catalyst, solvent (alcohol) and unsaturated compound were shaken together in a stout bottle connected to a hydrogen pressure tank and the rate of hydrogen absorption was followed by the fall in the gage pressure (1 lb./sq. in. = 286 cc. of hydrogen at atmospheric pressure and 25°). The hydrogen was admitted to the reaction bottle, without first removing the air, so that the gage pressure measured the partial pressure of hydrogen above the alcohol. The absorptions were mostly so rapid that it seemed unlikely that much air or alcohol vapor could penetrate from the bottle to the tank against the inrushing hydrogen. Platinum-oxide platinum black was used, prepared according to the directions of Adams and Shriner[6] (fusion at about 500°); 150 cc. of reagent alcohol (No. 25 denatured, 95% ethanol and 5% methanol) was used in each experiment.

In any one experiment on the hydrogenation of an olefin, the rate of hydrogen absorption, after a short period from the beginning, remained fairly constant until hydrogen practically equivalent to the olefin had been absorbed.[7] This is shown by the linear form of the curves in Fig. 1.

The relationship between the magnitude of these uniform absorption rates and the quantity of catalyst can be seen from Table I, columns 2

[4] Davis and Crandall, THIS JOURNAL, **52**, 3757, 3769 (1930).

[5] Purchased from the Burgess–Parr Co.

[6] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[7] Numerous observers have pointed out this striking fact; see Lebedev, Kobliansky and Yakubschik, *J. Chem. Soc.*, 418 (1925).

and 6. The absorption rate increased from zero, at first in proportion to the quantity of catalyst, but evidently tended toward a maximum value which would have been unchanged by the addition of more catalyst.

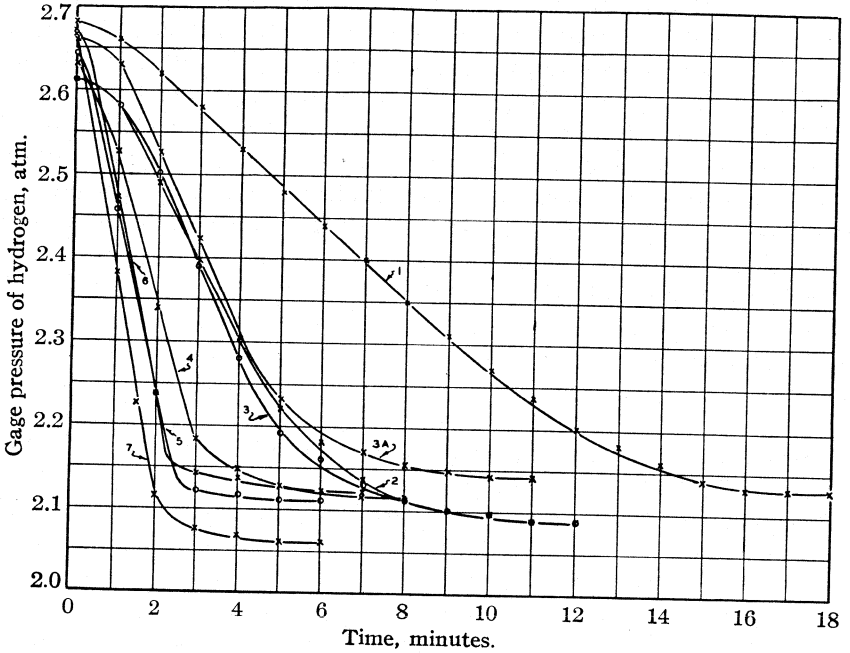


Fig. 1.—Hydrogenation of 10 cc. of 2-pentene in 150 cc. of alcohol, shaken 260 times per min. with various quantities of catalyst: (1) 0.03 g., (2) 0.07 g., (3) 0.10 g., (3A) 0.10 g., (4) 0.20 g., (5) 0.40 g., (6) 0.60 g., (7) 0.90 g.; average hydrogen pressure (gage), 2.4 atm.

In diffusing from the gas–liquid interface to the liquid–solid interface, the dissolved hydrogen must pass through two liquid stationary films by diffusion and the total drop in its concentration between the two interfaces is utilized in driving the dissolved gas through these films.

Let C_i = concn. of dissolved hydrogen at gas–liquid interface
$C_{cat.}$ = concn. of dissolved hydrogen at liquid–solid interface
R_1 = total resistance, to diffusion, of the liquid stationary film at gas–liquid interface
r_2/W = total resistance, to diffusion, of liquid stationary film at liquid–solid interface (W = g. of catalyst, r_2 = resistance per 1 g. of catalyst)
ρ = rate of hydrogen absorption (total)
K = a constant

$$\text{Then } \rho = K \frac{C_i - C_{cat.}}{R_1 + \frac{r_2}{W}} \qquad (1)$$

$$\frac{1}{\rho} = \frac{1}{K(C_i - C_{cat.})} \left(R_1 + \frac{r_2}{W}\right)$$

At a fixed rate of shaking R_1 remains unchanged and, for the same lot of catalyst, r_2 is constant. If, finally, the variations in $C_{cat.}$ are negligible compared to $C_1 - C_{cat.}$ then

$$\frac{1}{\rho} = \text{Const.} + \text{Const.} \left(\frac{1}{W}\right) \qquad (2)$$

Accordingly if $1/\rho$ is plotted against $1/W$, a straight line should result. In Fig. 2 the data from experiments with different quantities of catalyst are plotted in this way for three olefins, trimethylethene, 2-pentene and isopropylethene. For the first two, the points lie quite well on straight lines. In the case of isopropylethene, the second and fifth points are off from, but on opposite sides of, the straight line representative of the other five points. Apparently this is due to experimental errors.

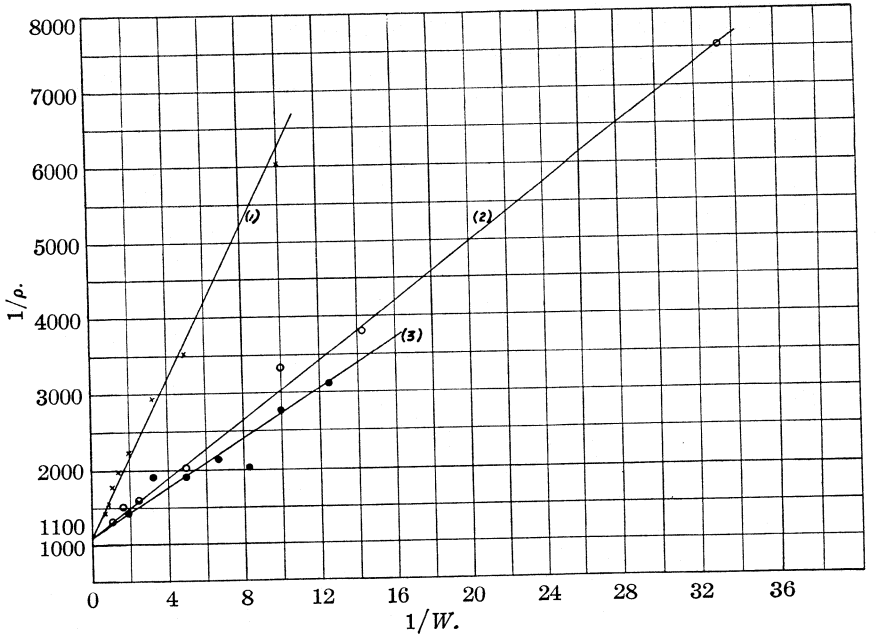


Fig. 2.—ρ = rate of hydrogen absorption, over period of uniformity, in mole/sec.; W = weight of catalyst in grams; (1), trimethylethene; (2), 2-pentene; (3), isopropylethene; average hydrogen pressure (gage) 2.4 atm.; shaking rate 260 times per min.; 150 cc. of alcohol + 10 cc. of hydrocarbon.

Within the accuracy of the data, all three curves converge to the same point at $1/W = 0$ or $W = \infty$. The corresponding value for ρ is 9.1×10^{-4} mole/sec. Under these conditions the concentration of dissolved hydrogen in the main body of the liquid has become equal to $C_{cat.}$ and the full drop in concentration $C_i - C_{cat.}$ is utilized in driving dissolved hydrogen through the liquid stationary film at the gas–liquid interface.

The resistances of the two liquid stationary films will be equal ($R_1 = r_2/W$) when the absorption rate is just half the above maximum. The quantity of catalyst corresponding to this condition can be obtained, for each series, from the curves of Fig. 2. Having these values for W, it is now possible to calculate the ratios of the total resistances, $R_1 + r_2/W$, and finally the ratios of the hydrogen absorption rates, for different quantities of catalyst, Table I. The agreement between the calculated and the experimental ratios of the absorption rates is rather striking (last two columns).

Furthermore, it is calculated (by means of equation 3 below) that in the 2-pentene experiments, Table I, for 0.03 g. of catalyst, the main body

TABLE I

HYDROGENATIONS OF OLEFINS (10 CC. IN 150 CC. OF ALCOHOL) WITH DIFFERENT QUANTITIES OF CATALYST. RATE OF SHAKING, 260 TIMES PER MINUTE

No.	W	Ratios: R_1 ratios	Ratios: r_2/W ratios	Ratios: $R_1 + r_2/W$ ratios	ρ mole $\times 10^4$/sec.	ρ ratios: Calcd.	ρ ratios: Exptl.
			Trimethylethene				
1	0.1 g.	1	4.8	5.8	1.62	1	1
2	.2	1	2.4	3.4	2.83	1.7	1.8
3	.3	1	1.6	2.6	3.40	2.2	2.1
(3a)	(.48)[a]	(1)	(1)	(2.0)	(4.55)	(2.9)	(2.8)
4	.5	1	0.96	1.96	4.50	3.0	2.8
5	.7	1	.69	1.69	5.28	3.4	3.3
6	.9	1	.53	1.53	5.73	3.8	3.5
7	1.1	1	.44	1.44	6.38	4.0	3.9
8	1.4	1	.34	1.34	6.52	4.3	4.0
9	∞	1	0.0	1.0	(9.1)	5.8	(5.6)
			2-Pentene				
1	0.03 g.	1	5.8	6.8	1.27	1	1
2	.07	1	2.5	3.5	2.54	2.0	2.0
3	.10	1	1.8	2.8	2.90	2.4	2.3
3a	(.175)[a]	(1)	(1)	(2)	(4.55)	(3.4)	(3.6)
4	.20	1	0.88	1.88	4.85	3.6	3.8
5	.4	1	.44	1.44	6.25	4.7	4.9
6	.6	1	.29	1.29	6.73	5.3	5.3
7	.9	1	.20	1.20	7.30	5.7	5.8
8	∞	1	.0	1.00	(9.1)	6.8	(7.2)
			Isopropylethene				
1	0.08 g.	1	1.9	2.9	3.22	1	1
2	.10	1	1.5	2.5	3.61	1.2	1.1
3	.12	1	1.25	2.25	4.97	1.3	1.5
4	(.15)[a]	(1)	(1)	(2)	(4.68)	(1.5)	(1.5)
5	.20	1	0.75	1.75	5.27	1.7	1.6
6	.3	1	.50	1.50	5.27	1.9	1.6
7	.5	1	.30	1.30	7.02	2.2	2.2
8	∞	1	.0	1.0	(9.1)	2.9	(2.8)

[a] From the curve of Fig. 2.

of the solution was 86% saturated with hydrogen, and for 0.9 g. only 20%. Since, as shown by Fig. 2 and Table I, $(C_1 - C_{cat.})$ remained substantially constant, then $C_{cat.}$ must have remained either constant, unaffected by large changes in the concentration of dissolved hydrogen in the main body of the liquid, or was negligible. If it was negligible, then the limiting rate of absorption reached with an infinite quantity of catalyst should be equal to the initial rate of hydrogen absorption by the solution. To test this conclusion, the rate of physical solution of hydrogen by alcohol in this apparatus was actually measured in the following way.

The bottle containing 150 cc. of alcohol, without any catalyst or olefin, was evacuated to a pressure of 8–10 cm. of mercury and shaken for several minutes to remove dissolved gases. Then with the bottle at rest, hydrogen was admitted to a total pressure of about 1.9 atm. The pressure was registered by the height of the mercury level in a capillary tube dipping into mercury in a closed bottle, 3 cm. in diameter, which sustained the full hydrogen pressure.

With the liquid at rest, the rate of hydrogen absorption was fairly slow; but when shaking started it was rapid, although by no means immeasurable. A fraction of a second was required to start the shaking, so that measurements were taken after the motor was almost up to speed (260 ± 5 shakings per min.). Then the time was determined for the first 2 cm. drop in the mercury pressure out of the last 4 cm., that is, the time required for solution of half the hydrogen still undissolved. Two observers were required. One started the shaking, the other measured the time. To accomplish this, a moving paper was drawn against a pencil, rotating uniformly eleven times per second, when the mercury level reached a fixed mark and withdrawn when it had fallen 2 cm. more. The following were the numbers of the pencil marks in five successive tests: 10, 9, 9, 10, 10. Average, 9.6, corresponding to 0.87 sec.

Let U = The unsaturation of the alcohol in regard to dissolved hydrogen at time t (sec.) expressed as the moles of the gas (in addition to that already dissolved) necessary to saturate the alcohol

$$\text{Then } -\frac{dU}{dt} = \text{Const. } U \qquad (3)$$

$$\text{and Const. } = \frac{1}{t} \ln \frac{U_0}{U}$$

$$\text{If } t_{0.5} = \text{time for a fall of 50\% in } U, \text{ then } -\frac{dU_0}{dt} = \frac{0.693\,U_0}{t_{0.5}}$$

This relationship holds whatever the value of U, but if the readings could be started before any hydrogen was dissolved, then U_0 would be equal to the total quantity of hydrogen soluble, at this pressure, in the alcohol; 150 cc. of alcohol would dissolve about 1.27×10^{-3} mole of hydrogen at 2.4 atmospheres. Accordingly the initial rate of solution of hydrogen in this quantity of alcohol in our hydrogenation experiments (Adams apparatus, hydrogen pressure 2.4 atm., and shaking rate (260 ± 5) times per min.) would be $(0.693/0.87) \times 1.27 \times 10^{-3} = 10 \times 10^{-4}$ mole/sec.

More than a year later the experiments (first series) were repeated, another observer replacing one of the first two (second series).

COLLECTED RESULTS ON THE INITIAL RATE OF HYDROGEN SOLUTION (AT 2.4 ATM. OF HYDROGEN) BY 150 CC. OF LIQUID SHAKEN 260 ± 5 TIMES PER MINUTE IN THE ADAMS APPARATUS

1st Series, alcohol only	10×10^{-4} mole/sec.
2d Series, alcohol only	11.5×10^{-4} mole/sec.
2d Series, alcohol 10 cc. 2-pentene	9.6×10^{-4} mole/sec.
2d Series, alcohol 10 cc. trimethylethene	9.0×10^{-4} mole/sec.

The absorption rate for an infinite quantity of catalyst, 9.1×10^{-4} mole/sec. of hydrogen, was therefore approximately equal to the initial rate of physical solution of the hydrogen. The concentration of dissolved hydrogen in the liquid at the liquid–solid interface, $C_{cat.}$, must have been low in all our hydrogenation experiments.[8]

If these explanations are correct, then with a fixed rate of shaking the changes in the hydrogen absorption rate with the quantity of catalyst are caused by changes in the total resistance, r_2/W, of the liquid stationary film at the liquid–solid interface. On the other hand, one hydrogenation at a faster shaking rate (430 times per min. using 2-pentene and 0.6 g. of catalyst) gave an absorption rate 9.2×10^{-4} mole/sec. of hydrogen, compared to only 6.7×10^{-4} at 260. Undoubtedly this higher rate corresponds mainly to an increased ease of physical solution of hydrogen in the alcohol. (R_1 was less.)

The *absorption rate per unit area of surface* could be calculated if the area of the gas–liquid interface of the shaken liquid were known. An estimate of this surface was made by measuring the rate of absorption of pure ethylene by 150 cc. of 95.8% sulfuric acid, when shaken in the apparatus, and dividing by the rate per unit area into the acid at rest (6×10^{-9} mole/sec.). This method is based on the postulate, which is supported by experimental evidence, that the absorption rate of ethylene per unit area of surface of this acid is unaffected by the rate of shaking.[9]

Rate of shaking per min.	260	420
Over-all ethylene absorption rate, moles per sec.	24000×10^{-9}	28000×10^{-9}
Calculated area of liquid surface, sq. cm.	4000	4700

[8] Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923), using a similar method of hydrogenation, studied the rates of the absorption during the reduction of aldehydes. Ferrous chloride was found to "promote" the reaction and, with a fixed quantity of catalyst, 0.23 g., the absorption rate increased with the quantity but approached a maximum asymptotically which was practically attained with 0.001 mole of the iron salt. On the other hand, using 0.001 mole of ferrous chloride, but changing the quantity of catalyst, the absorption rates increased in the same manner as those in Table I, and the rate with 0.23 g. of catalyst (4×10^{-4} mole/sec. of hydrogen) was evidently approaching the maximum that could be obtained with the quantity of alcohol, 50 cc., and the shaking rate (260 ± 5 times per min.) employed. Further, the fact that this rate is about half the maximum in our experiments where three times as much alcohol was used, indicates that $C_{cat.}$ was low in their experiments also.

[9] Davis and Crandall, THIS JOURNAL, **52**, 3781–3782 (1930).

The maximum rate of absorption during the hydrogenation experiments (Table I) would, therefore, be 2.3×10^{-7} mole/sec. per sq. cm.[10]

In a former communication,[11] some evidence has been given that the resistances to solute diffusion (per unit area of interface) through the liquid stationary films at the gas–liquid interface and liquid–solid interface are of the same order. If they are assumed to be *equal*, then it would follow that when their total resistances are the same ($R_1 = r_2/W$), the areas of the two interfaces are also equal. Taking 4000 sq. cm. for the area of the gas–liquid interface in the experiments summarized in Table I, it can now be calculated from the weights of catalyst having an equal film resistance that the average diameters of the platinum particles (if spherical) in the three series of experiments were as follows, trimethylethene series 0.34×10^{-4} cm., 2-pentene series 0.12×10^{-4} cm. and isopropylethene series 0.11×10^{-4} cm. This is in qualitative agreement with the values 0.3 to 1×10^{-4} cm. obtained by Taylor, Kistiakowsky and Perry[12] from direct measurements of the average sizes of the particles in platinum black catalyst prepared by three different methods.

A new lot of catalyst was used in each series shown in Fig. 2 but possibly the differences in the slopes of these curves are not caused entirely by variations in the particle size of the catalyst. The bases for these calculations of surface areas and particle sizes are only approximate. However, the qualitative agreement of the calculations with the above-mentioned direct measurements substantiates the theory of the part played by the liquid stationary films in these hydrogenations. More accurate methods of experimentation will be necessary for determining whether all curves extrapolate to exactly the same point at $1/W = 0$, and whether the differences in the slopes are entirely due to variation in the particle size.

The Adams apparatus is not suitable for testing these questions, mainly because the rate of hydrogen solution is very high (the exact purpose of its design). One needs a large body of liquid, moderately stirred, and having only a small liquid–gas interface. Under the latter conditions the time necessary to half saturate the alcohol with hydrogen might become a matter of minutes, instead of less than one second as was the case in our experiments. Absorption rates under various conditions could then be followed accurately.

[10] Conant and Scherp, THIS JOURNAL, **52**, 3764 (1930), measured the rate of hydrogen solution by tetrachloroethane shaken 250 times per minute. The initial rate at 2.4 atm. has been calculated from their data to be 2.1×10^{-7} mole per sec. per sq. cm. (The solubility of hydrogen in tetrachloroethane is about 15% lower than in alcohol.)

[11] Davis and Crandall, *ibid.*, **52**, 3761 (1930).

[12] Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 749 (1930). The experiments of Bredig and Allolio, *Z. physik. Chem.*, **126**, 41–47 (1927), showed that the particles in the Adams catalyst are also minute.

The Relative Rates of Hydrogenation of the Components in Mixtures of Olefins.—Lebedev and his co-workers[13] have concluded that olefinic compounds of different types of substitution are hydrogenated consecutively and selectively, in the presence of colloidal platinum, that is to say, in general, one compound is almost completely hydrogenated before the next is attacked.

However, in no case in their experiments were the products from a partial hydrogenation of a mixture of two compounds analyzed by methods entirely independent of their hydrogenation hypotheses. And mostly the products were not analyzed at all, the conclusions being drawn from breaks which appeared in the curves of the rates of hydrogen absorption, which, as pointed out by Lebedev, are not sharp. Furthermore, in many cases there is no rigorous proof of the order of hydrogenation.

They also measured the hydrogen absorption rates for single ethylenic compounds at atmospheric temperature and pressure employing approximately 0.01 mole of the compound, in 10–15 cc. of alcohol with 0.05 to 0.3 g. of catalyst or in a few cases even greater amounts. The averages of the values for the different types of compounds do not appear to be particularly significant. As calculated from their curves they are (expressed in moles of hydrogen per sec. $\times 10^3$) monosubstituted 11, *sym.*-disubstituted 7, *unsym.*-disubstituted 10 and tri- and tetrasubstituted 6.

They state that "in general the effect of doubling the concentration of catalyst in a given case was to increase the rate of absorption of hydrogen by about 50%." On our hypotheses this would indicate relative values for R and r_2/W in their experiments 1 and 2.

Adkins, Diwoky and Broderick,[14] concluded that "the relative ease of reduction of two substances in a mixture may not be certainly determined even qualitatively by determining the rates of reduction of the two substances separately." They measured rates of reduction by the periods required for complete reduction of the compounds under similar conditions. However, these periods are perhaps not so significant as the rates of hydrogen absorption, while still fairly uniform. The rate nearly always falls off near the end of the reduction. Further, Thomson (unpublished data) has shown that the period required to completely reduce olefins depends greatly on their peroxide content.

The writers have, therefore, half hydrogenated four different mixtures of two olefins of different types of substitution and have analyzed the products by methods entirely independent of hydrogenation. The limited experimental data (Table II) indicate that in hydrogenation of mixtures of olefins, as pointed out by Vavon[15] and Lebedev,[13] the order of reduc-

[13] Lebedev and others, *J. Chem. Soc.*, 417–440 (1925); 823–837, 2190–2204 (1928); 220–225 (1929); 321–336 (1930).

[14] Adkins, Diwoky and Broderick, THIS JOURNAL, **51**, 3423 (1929).

[15] Vavon and Kleiner, *Compt. rend.*, **177**, 401 (1922).

tion is as follows: monosubstituted, disubstituted, trisubstituted. However, the more rapidly reacting constituent was not hydrogenated to the exclusion of the other component, since in all cases there was an appreciable quantity of the latter reduced.

Synthetic mixtures of two pure olefins in approximately equal molecular proportions were hydrogenated until 50% or somewhat more of the total had been converted to paraffins. The proportion of each olefin left unchanged in the mixture was then determined by analysis.

In the case of the first mixture, propene and 2-butene, a 5-liter flask was used the neck of which had been drawn down and a stopcock sealed thereto. The alcohol and catalyst were placed inside, the flask was evacuated and the gas mixture, 0.12 mole of hydrogen and 0.078 mole of each olefin, drawn in. The other experiments, 2, 3 and 4, were carried out in the Adams apparatus already described. The olefins were here measured out in the liquid state, the quantities being checked both by weight and by volume and were poured directly into the chilled reagent alcohol (150 cc.).

As will be seen from Table II, there was a considerable difference between the boiling points of the two olefins chosen for each mixture so that fractional distillation could be utilized in the analyses of the products. By means of a vacuum-jacketed column containing a glass spiral with forty turns,[16] the

TABLE II

COMPETITIVE HYDROGENATIONS OF MIXTURES OF TWO OLEFINS

The corresponding paraffin formed by hydrogenation is given under each olefin in parentheses.

No.	Olefins, paraffin product	B. p., °C.	Formula and type of olefin	Mole in original mixture	% of olefin hydrogenated
I	Propene	−47.5	$CH_3CH=CH_2$ Monosubstituted	0.078	90
	(Propane)	(−44.5)			
	2-Butene	1.5–1.7	$CH_3CH=CHCH_3$ *Sym.*-disubstituted	.078	20
	(*n*-butane)	(0.6)			
II	1 Butene	−6.3—5.1	$CH_3CH_2CH=CH_3$ Monosubstituted	.040	79
	(*n*-butane)	(0.6)			
	2-Pentene	36.3–36.5	$CH_3CH_2CH=CHCH_3$ *Sym.*-disubstituted	.051	21
	(*n*-pentane)	(36.2)			
III	Isobutene	−7.0—6.9	$(CH_3)_2C=CH_2$ *Unsym.*-disubstituted	.0485	96
	(Isobutane)	(−10.2)			
	Trimethylethene	38.2–38.4	$(CH_3)_2C=CHCH_3$ Trisubstituted	.0530	44
	(Isopentane)	(28)			
IV	Isopropylethene	20.1–20.4	$(CH_3)_2CH_2CH=CH_2$ Monosubstituted	.044	93
	(Isopentane)	(28.0)			
	Trimethylethene	38.2–38.4	$(CH_3)_2C=CHCH_3$ Trisubstituted	.044	20
	(Isopentane)	(28.0)			

[16] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

mixtures of unchanged olefins and their hydrogenation products were easily separated from the alcohol and were refractionated several times from metallic sodium. Although the quantity of liquid hydrocarbon was in no case greater than 12 cc., it readily separated, in the first three experiments, into two sharply differentiated fractions each of which boiled over the range of one olefin and its corresponding paraffin. The product from No. 4 was more difficult to fractionate because both olefins yield the same paraffin, isopentane, which boils about half-way between them.

The composition of the separate fractions was then determined by chemical tests.[17]

Summary

1. A study of the rates of catalytic hydrogenation of three olefins has been made. The results have been examined in the light of the theory that the rate of hydrogen absorption is controlled by the rate of diffusion of hydrogen through liquid stationary films at the gas–liquid and liquid–solid interfaces.

2. The ratios of the hydrogen absorption rates for different quantities of catalyst, in three series of experiments with different olefins, have been calculated from this theory and agreed very well with those determined experimentally.

3. The value of the absorption rate with an infinite quantity of catalyst (obtained by extrapolation) agreed with an approximate value found, by direct measurements, for the initial rate of absorption of hydrogen in alcohol, and in alcohol solutions of olefins, under similar conditions.

4. The average area of gas–liquid interface during these hydrogenations has been determined and, with the aid of this value, the particle size of the catalysts calculated.

5. The relative proportions of two olefins reacting during partial hydrogenation of an equimolecular mixture of the two have been measured for four different mixtures. The products were analyzed by methods independent of hydrogenation.

CAMBRIDGE, MASSACHUSETTS

[17] Davis and Daugherty, *Ind. Eng. Chem., Anal. Ed.*, **4**, 193 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE CHEMICAL KINETICS OF HIGH VALENCE TYPE ELECTROLYTES IN DILUTE AQUEOUS SOLUTIONS

BY VICTOR K. LA MER AND R. W. FESSENDEN[1]

RECEIVED MARCH 2, 1932 PUBLISHED JUNE 6, 1932

Introduction

In developing the theory of chemical reaction velocity in solution and particularly to account for the anomaly known as neutral salt effect, Brönsted[2] postulates that the reaction mechanism involves a series of intermediate unstable complexes. The rate of transformation of the most unstable complex, designated as X, determines the tempo of the reaction. For the velocity of a bimolecular reaction like

$$A + B \rightleftharpoons X \longrightarrow R_1 + R_2 + \ldots \qquad (1)$$

he gives the expression

$$\frac{dx}{dt} = k_0 C_A C_B f_A f_B / f_x \qquad (2)$$

Here the factor, $F = f_A f_B / f_x$, representing the ratio of the activity coefficients is introduced as a correction to the classical expression valid for ideal solutes to account for the changes in velocity resulting from a change in the nature of the medium. Such environmental changes are produced by variation in the concentrations of the reactants or by the addition of chemically inert substances. It is important to subject the theory to a critical analysis to ascertain whether the introduction of activity coefficients, thermodynamic quantities which are independent of time, furnishes a sufficient correction. In a recent paper from this Laboratory[3] it was shown that the further assumption of a change in the degree of orientation of complex molecules on collision was necessary to account for the results for specially selected examples.

For an unequivocal test of the theory, it is necessary to measure these activity coefficients in precisely the same medium in which the reaction proceeds. The instability of A and B in the presence of each other frustrates such measurements. However, the theory can be tested by comparing the observed behavior of the factor, F, on changing concentration with predictions based upon measurements of stable ions of the same electric charge type. For this purpose, it has been customary to employ the

[1] This paper is from a dissertation submitted in July, 1931, by R. W. Fessenden to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. It was presented at the Symposium on Kinetics of Homogeneous Reactions at the Buffalo (September, 1931) meeting of The American Chemical Society.

[2] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925). A critical review and summary are given by La Mer, *Chem. Rev.*, **10**, 179 (1932).

[3] La Mer and Kamner, THIS JOURNAL, **53**, 2832 (1931).

Debye–Hückel limiting law to predict the kinetic behavior.[4] Solubility studies,[5,6,7] however, have demonstrated that this simple law does not hold when the product of the charges of the ions of opposite sign is greater than four. Instead the solubility measurements have revealed a characteristic behavior which has proved to be at variance with the predictions of the theory as developed by Debye and Hückel but not inconsistent with the fundamental postulates of the theory provided a more complete mathematical solution of the Poisson–Boltzmann equation is employed.[8]

For example, the reaction

$$BrCH_2COO^- + S_2O_3^= \rightleftharpoons [X^=] \longrightarrow S_2O_3CH_2COO^- + Br^- \qquad (3)$$

involves a critical complex with three negative charges. If the reactants are introduced in the form of their sodium salts, the valence product of ions of opposite sign does not exceed three for any pair in the mixture. Under such conditions the observed rate agrees[9] with the predictions of the equation

$$\log k = \log k_0 + Z_A Z_B \sqrt{\mu} \qquad (4)$$

obtained by introducing the Debye–Hückel limiting law

$$-\log f_i = -0.50\, Z_i^2 \sqrt{\mu} \qquad (5)$$

into equation (2) and integrating on the assumption that the ionic strength, μ, remains unchanged during the course of the reaction. On the other hand, if the reactants are introduced in the form of their calcium, barium or magnesium salts, there will be ionic pairs involving the critical complex with a valence product equal to six. When bivalent cations are present, equations (5) and (4) will not be obeyed. However, if equation (2) is correct, we should expect the curves obtained on plotting the logarithm of the velocity constant against the square root of the ionic strength to have a form practically identical with those obtained by La Mer and Mason for the solubility of salts of the same valence type. The essential characteristic is an experimental limiting slope two to three times that predicted by the Debye–Hückel limiting law for the region 0.001μ to 0.01μ; and a point of inflection so that the limiting law is obeyed at extreme dilution.

The reaction between bromoacetate ion and the thiosulfate ion has been studied previously by Slator,[10] Krapivin,[11] La Mer[9] and Kappanna.[12] It is free from interfering side reactions since the constant for the hy-

[4] Brönsted and Livingston, THIS JOURNAL, **49**, 435 (1927).

[5] La Mer and Mason, *ibid.*, **49**, 410 (1927).

[6] La Mer and Cook, *ibid.*, **51**, 2622 (1929).

[7] La Mer and Goldman, *ibid.*, **51**, 2632 (1929).

[8] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931). Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[9] La Mer, THIS JOURNAL, **51**, 3341 (1929).

[10] Slator, *J. Chem. Soc.*, **87**, 481 (1905).

[11] Krapivin, *Z. physik. Chem.*, **82**, 439 (1913).

[12] Kappanna, *J. Indian Chem. Soc.*, **6**, 45 (1929).

drolysis of the bromoacetate ion to the glycolate ion with the formation of the hydrogen ion and the bromide ion

$$BrCH_2COO^- + H_2O \longrightarrow H^+ + Br^- + CH_2OHCOO^-$$

is of the negligible order[3] of 1×10^{-6}. There is no change in ionic strength as the reaction proceeds. It can be followed precisely by iodine titration even at great dilution.

In studying the effect of changing ionic environment upon this reaction two methods may be used. (*a*) The total ionic concentration may be changed by varying only the concentration of the reacting salts. (*b*) Neutral salts may be added to a fixed concentration of reactants. Method (*a*) is the simpler because only one cation and no foreign anions need be present in addition to the anions of the kinetic reaction. Method (*b*) has the objection that at least one foreign cation or anion must be introduced into the mixture. It is also not well adapted for work at very small concentrations since it is not possible to have a reasonable concentration of reactants and at the same time keep the ratio of added salts to reactants large. Method (*a*) was therefore adopted except for the studies with the lanthanum salts.

II. Preparation of Materials

Bromoacetic Acid.—Kahlbaum's bromoacetic acid was redistilled under reduced pressure (10 mm.). The bromine content of the purified acid was 99.5% of the theoretical value. Its acid titration value agreed with the theoretical within 1 part per thousand. When 0.0333 *M* bromoacetate was treated with 0.0666 *M* thiosulfate, 99.7% of the theoretical amount of the thiosulfate reacted in forty-eight hours. At these concentrations the reaction should have been completed to within 1 part per thousand in twelve hours. We may therefore safely assume a purity between 99.5–99.7%. The bromoacetic acid was kept in a desiccator over sulfuric acid in a dark bottle and closet.

Sodium and Potassium Thiosulfate.—The C. P. salts were recrystallized from distilled water.

Barium Thiosulfate.—C. P. barium thiosulfate was recrystallized from distilled water. Since this salt is only slightly soluble in water a saturated solution was prepared at 100°. After cooling to 15°, the crystals were filtered off and dried at room temperature.

Magnesium thiosulfate was prepared by a modification of the method of Rammelsberg.[13] Sulfur dioxide was passed into a suspension of 100 g. of magnesium oxide in 300 cc. of water until the mixture was slightly acid to litmus. An excess of sulfur was added together with sufficient water to make the total volume one liter. The mixture was boiled for four hours, replacing the water evaporated from time to time. The clear solution was decanted through a filter and allowed to cool. The magnesium thiosulfate was then precipitated by adding alcohol. The product was twice recrystallized from distilled water. In recrystallizing the magnesium thiosulfate it was found that a slight decomposition occurred if the solution was heated. Accordingly the crystals were dissolved in water without heating and the solution was allowed to evaporate at room temperature.

Calcium Thiosulfate.—The method was the same as that used for the magnesium salt.

Sodium Hydroxide.—Sticks of electrolytic sodium hydroxide were rinsed with distilled water and dissolved in freshly boiled water. The solutions were kept in paraffin-

[13] Rammelsberg, *Pogg. Ann.*, Second Series, **56**, 295 (1842).

coated bottles and protected from carbon dioxide by guard tubes of soda lime. The solutions were standardized against Bureau of Standards potassium acid phthalate using phenolphthalein as an indicator.

Potassium Hydroxide.—Electrolytic potassium hydroxide was used in making up solutions. The same procedure was followed as in the preparation of sodium hydroxide solutions.

Barium Hydroxide.—Solutions were prepared from C. P. barium hydroxide by the method given by Findlay.[14]

Calcium Hydroxide.—A suspension of calcium hydroxide was prepared from C. P. calcium chloride by treating a solution of the chloride with an equivalent amount of sodium hydroxide solution. The precipitate was washed by decantation until the clear supernatant solution gave no test for the chloride ion after acidification with nitric acid and the addition of silver nitrate.

Magnesium Hydroxide.—A suspension of the hydroxide was prepared from C. P. magnesium chloride by the method used for the preparation of calcium hydroxide.

Iodine.—Commercial resublimed iodine was used without further purification. All iodine solutions were made up with 4% potassium iodide and standardized against arsenious acid.

Potassium Iodide.—Merck's potassium iodide was used. Samples gave no color with starch in neutral solution after twenty-four hours in the dark and no color with starch after acidification.

Arsenious Acid.—Kahlbaum's "zur Analyse" arsenious oxide was used as a primary standard. Solutions were prepared after the method of Kolthoff,[15] and Washburn's[16] procedure was followed in titration using a sodium bicarbonate buffer.

Nitrogen.—Commercial nitrogen was passed through a solution of potassium pyrogallate to remove traces of oxygen, and next over heated copper gauze to remove any carbon monoxide formed. The gas was then washed with water and passed through a sample of the solution to be used before passing it into the reaction mixture.

Lanthanum Chloride.—A sample of cerium-free lanthanum chloride prepared by the Welsbach Company was used.[7]

All volumetric glassware was calibrated, and the distilled water boiled previous to use to remove oxygen and destroy microörganisms, which interfere with the stability of thiosulfate solutions.

III. Experimental Procedure

All velocity experiments were conducted at 25.00 ± 0.02°. The setting of the Beckmann thermometer was checked against a thermometer calibrated by the Bureau of Standards.

The thiosulfate solutions were titrated with a standard iodine solution and adjusted to the exact concentration desired. The bromoacetate solutions were prepared by weighing out the required amounts of bromoacetic acid and neutralizing with the hydroxides of the various metals using phenolphthalein as an indicator. Standard solutions of the soluble hydroxides were used as a check on the weighing. If the hydroxide was insoluble a suspension was used. After neutralization the solutions were diluted to the desired volume. In making up the reaction mixtures solutions of thiosulfate and bromoacetate were freshly prepared and standardized just before use.

[14] Findlay, "Practical Physical Chemistry," Longmans, Green and Company, 1925, p. 145.

[15] Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, 1929, p. 354.

[16] Washburn, THIS JOURNAL, **30**, 31 (1908).

Experiments were carried out as follows. The two solutions containing the reactants were placed in the thermostat. When they had reached the temperature of the bath, the reactants were pipetted into the reaction vessel, taking the time of half delivery of the pipet when adding the second component as the initial time of the reaction. The very dilute reaction mixtures were prepared by diluting measured amounts of 0.01 M solutions of the reactants to the required volume in volumetric flasks and then transferred to the reaction vessel. At suitable intervals aliquots of the mixture were withdrawn and titrated with iodine. In experiments at the higher concentrations (0.01 M or greater), where the time error in stopping the reaction becomes important, the aliquot of the reaction mixture was pipetted into an amount of the iodine solution just insufficient to react with all the thiosulfate present in the sample. The conversion of the greater part of the reacting thiosulfate by the iodine effectively stopped the reaction. The titration was then completed by adding the standard iodine solution from a buret as quickly as possible. The dilute solutions in which the time error was small were titrated by introducing all the standard iodine directly into the aliquot of the reaction mixture.

The velocity constants were calculated by the formula $k = \frac{1}{a}\frac{1}{t}\frac{x}{(a-x)}$ where k is the velocity constant; t is the time in minutes; a is the initial concentration of the reactants in moles per liter; and x is the amount changed in time t. The value of a was determined by the dilution of the standard solutions used in making up the reaction mixtures and is expressed in moles per liter. The values of x and $(a-x)$ in the ratio were determined in terms of the volume of iodine solution used in titrating the reaction mixtures since these values do not need to be in absolute units as is necessary for the quantity $1/a$.

IV. Analytical Precision

In titrating the most dilute thiosulfate solutions there is a perceptible error in detecting the starch–iodine end-point which was corrected by appropriate blanks. Kolthoff[15] states that 1×10^{-5} M of iodine per liter is required to give the blue color with starch in the presence of 4×10^{-5} M of I^- per liter. The sensitivity increases on increasing the iodide concentration. In this work the concentration of I^- ion at the end-point of the titration was always greater than 0.01 M. With this concentration of I^- ion the test was found in a north light to be sensitive to 1.5×10^{-6} M of iodine per liter in a volume of 250 cc.

In titrating iodine with thiosulfate in very dilute neutral solutions, Kolthoff[15] states that iodine is hydrolyzed to hypoiodite which oxidizes the thiosulfate to sulfate instead of to tetrathionate. This mechanism requires less thiosulfate than the normal reaction. He states that the reverse titration, that of thiosulfate with iodine, proceeds normally since the iodine is removed at once and has no opportunity to enter into the hydrolytic side reaction. Before we were acquainted with this explanation, experiments had been carried out to test the reliability of the procedure by adding iodine to the reaction mixture and then back-titrating with thiosulfate. In experiments at a concentration of 0.001 M it was found that the velocity constants varied with the volume of solution in which the titration was performed. In titrating directly with iodine no difference was detected on varying the volume. The results for the di-

rect titration were somewhat higher than for the back titration. At concentrations of 0.002 M and greater no difference in the velocity constants was produced by changing the order of adding the reagents in the titration.

V. Stability of Thiosulfate Solutions

In very dilute solutions the stability of the thiosulfates may exercise a perceptible influence upon the results unless special precautions are taken. By preparing the solutions in freshly boiled water as recommended by Kilpatrick and Kilpatrick[17] we found that 0.01 M thiosulfate solutions retain their titer to within 0.1% for a period of one week. However, experiments in which the initial concentration of thiosulfate was of 0.001 M or less exhibited a slight increase in the velocity constants after a period of two days. This drift in the values of the constants may be due to decomposition of the thiosulfate, for the increase was accelerated by the addition of traces of cupric ion (1×10^{-6} M per liter) in agreement with the studies of Abel.[18]

On the other hand, velocity experiments at an initial concentration of 0.00025 M thiosulfate performed under an atmosphere of nitrogen instead of air gave excellent constants! A solution of 0.00025 M thiosulfate preserved under nitrogen also showed no change in the iodine titration after one week and a change of only 0.5% after two weeks. All velocity experiments with 0.001 M thiosulfate or less which continued for more than two days were accordingly carried out under nitrogen. Since no experiment was continued for more than ten days any decomposition of the thiosulfate was negligible. It is not certain whether the decomposition observed in the dilute thiosulfate solutions was due to a reaction between oxygen and thiosulfate induced by minute traces of ions such as cupric or ferric ion present as impurities in our distilled water or whether it was due to bacteria whose growth or action is inhibited by the removal of the oxygen. The important point is that the results in the presence of nitrogen were reproducible in highly dilute solution and the constants under these conditions showed no drift with time!

When it was necessary to use nitrogen in an experiment, the purified gas was bubbled through the reaction mixture for forty-five minutes or more at the start of the experiment to remove the oxygen. Nitrogen was bubbled through the mixture daily to remove any trace of oxygen present due to possible leakages. Samples of the solution were removed by a pressure of nitrogen. The reaction mixtures in experiments performed under nitrogen were kept in glass-stoppered flasks of the type designed by MacInnes and Dole[19] for work in an atmosphere of inert gas.

[17] M. J. Kilpatrick and M. L. Kilpatrick, THIS JOURNAL, **45**, 2131 (1923).

[18] Abel, *Ber.*, **56**, 1076 (1923).

[19] MacInnes and Dole, THIS JOURNAL, **51**, 1119 (1929).

VI. Experimental Results

To illustrate the character of the results three representative runs are included, one at each of the two lowest (0.00025 *M*) concentrations and one at the highest (0.05 *M*) concentration used.

EXPT. No. K 32. $a = b = 0.00025\ M$

100 ml. of 0.005 *M* $K_2S_2O_3$ No. 20 and 50 ml. of potassium bromoacetate 0.01 *M* No. 20. Made up to 2 liters in a volumetric flask. 200-ml. aliquots titrated with iodine No. 20. Nitrogen used. Blank on iodine in this volume, 0.28 ml.

t, min.	Titer, ml.	*x*	$a - x$	*k*
0	24.52			
2778	20.52	4.00	20.24	0.285
4500	18.53	5.99	18.23	.292
5886	17.24	7.28	16.96	.292
8456	15.40	9.12	15.12	.285
9867	14.40	10.12	14.12	.290
12727	12.86	11.66	12.58	.291
14445	12.07	12.45	11.79	.292

Average 0.289 ± 0.003

The identical Expt. No. K31 gave 0.288 ± 0.001

EXPT. No. Ba 6. $a = b = 0.0005\ M$

200 ml. of barium thiosulfate 0.005 *M* No. 2 and 100 ml. of barium bromoacetate 0.005 *M* No. 2. Made up to two liters in a volumetric flask. 200-ml. aliquots titrated with iodine No. 18. Nitrogen used. Blank on iodine in this volume, 0.20 ml.

t, min.	Titer, ml.	*x*	$a - x$	*k*
0	43.75			
1115	36.05	7.70	35.85	0.385
1355	34.79	8.96	34.59	.382
2418	30.11	13.64	29.91	.377
2545	29.58	14.17	29.38	.379
2704	28.92	14.83	28.72	.382
3885	25.33	18.42	25.13	.377
4128	24.70	19.05	24.50	.379

Average 0.380 ± 0.002

The identical Expt. No. Ba 5 gave 0.386 ± 0.001

EXPT. No. Na 6. $a = b = 0.0500\ M$

50 ml. of sodium thiosulfate 0.1 *M* and 50 ml. of sodium bromoacetate 0.1 *M*. 10-ml. aliquots titrated with iodine No. 8.

t, min.	*x*, ml.	$a - x$	*k*
0		27.90	
10	7.40	20.50	0.722
15	9.93	17.97	.736
20	11.74	16.16	.727
25	13.30	14.60	.728
30	14.58	13.32	.730
35	15.63	12.27	.728
40	16.53	11.37	.726
45	17.33	10.57	.729
51	18.19	9.71	.734

Average 0.729 ± 0.003

The deviations recorded are the average deviations from the arithmetical mean. This deviation was less than 1% except for three runs (Ba P8, Na P1 and K 32) and was considerably less at the higher concentrations.

The results of one hundred experiments are reported in Tables I and II. Some preliminary experiments performed in developing the method

TABLE I

THE EFFECT OF IONIC STRENGTH UPON THE VELOCITY OF THE THIOSULFATE–BROMOACETATE REACTION IN THE PRESENCE OF VARIOUS CATIONS

No.	C $a = b$	$\sqrt{\mu}$	k	log k (characteristic negative)	log k/k_0	$\frac{\log k/k_0}{2\sqrt{\mu}}$
			Potassium as Cation			
K 38	0.0333	0.365	0.697 ±0.0020	1.843	0.457	0.63
K 39	.0333	.365	.697 ± .002	1.843	.457	.63
K 23	.0250	.316	.657 ± .002	1.816	.433	.69
K 25	.0250	.316	.640 ± .002	1.806	.420	.66
K 26	.0250	.316	.630 ± .002	1.799	.413	.65
K 27	.0250	.316	.629 ± .002	1.799	.413	.65
K 4	.0200	.282	.598 ± .006	1.777	.391	.69
K 6	.0200	.282	.595 ± .003	1.775	.389	.69
K 5	.0100	.200	.491 ± .001	1.691	.305	.76
K 8	.0100	.200	.485 ± .002	1.686	.300	.75
K 9	.0050	.141	.427 ± .003	1.630	.244	.87
K 11	.0050	.141	.429 ± .003	1.632	.246	.87
K 17	.0050	.141	.431 ± .003	1.635	.249	.88
K 24	.0025	.100	.378 ± .001	1.578	.192	.96
K 28	.0025	.100	.371 ± .001	1.569	.183	.92
K 21	.0016	.080	.349 ± .001	1.543	.157	.98
K 18	.0016	.080	.350 ± .002	1.544	.158	.98
K 20	.0010	.0632	.334 ± .002	1.524	.138	1.04
K 29	.0010	.0632	.326 ± .001	1.513	.127	1.00
K 37	.00075	.0548	.313 ± .001	1.496	.110	1.00
K 22	.00050	.0447	.301 ± .003	1.479	.093	1.04
K 33	.00050	.0447	.295 ± .002	1.470	.084	0.94
K 34	.00050	.0447	.205 ± .002	1.470	.084	0.94
K 35	.00050	.0447	.300 ± .001	1.477	.091	1.02
K 36	.00050	.0447	.3003 ± .0007	1.4776	.092	1.03
K 31	.00025	.0316	.288 ± .001	1.459	.073	1.15
K 32	.00025	.0316	.289 ± .003	1.461	.075	1.18
K 1P	.0025	.100	.368 ± .003	1.566	.180	0.90
K 15	.0025	.100	.366 ± .004	1.563	.177	0.88
			Sodium as Cation			
Na 1	0.0250	0.316	0.590 ±0.003	1.771	0.385	0.61
Na 5	.0250	.316	.610 ± .001	1.785	.399	.63
Na 6	.0500	.447	.729 ± .003	1.863	.477	.53
Na 7	.0333	.365	.650 ± .0005	1.813	.427	.58
Na 3	.0100	.200	.477 ± .002	1.679	.293	.73
Na 4	.0050	.141	.415 ± .001	1.618	.232	.82
Na 2	.0025	.100	.377 ± .003	1.576	.190	.95
Na P1	.0025	.100	.377 ± .006	1.576	.190	.95

TABLE I (*Continued*)

No.	C $a = b$	$\sqrt{\mu}$	k	log k (characteristic negative)	log k/k_0	$\frac{\log k/k_0}{2\sqrt{\mu}}$
			Barium as Cation			
	μ = ionic strength = 5.5 a. $a = b$ = mole/liter of reacting ions					
Ba 2	0.0075	0.203	0.696 ±0.001	1.843	0.457	1.13
Ba 1	.0050	.166	.632 ± .001	1.801	.415	1.25
Ba P4	.0050	.166	.629 ± .005	1.799	.413	1.24
Ba 10	.0020	.105	.522 ± .002	1.718	.332	1.58
Ba P8	.0020	.105	.522 ± .007	1.718	.332	1.58
Ba 4	.0010	.0742	.456 ± .002	1.659	.273	1.84
Ba 7	.0010	.0742	.416 ± .012	1.649	.263	1.77
Ba 5	.0005	.0520	.386 ± .001	1.587	.201	1.93
Ba 6	.0005	.0520	.380 ± .002	1.580	.194	1.87
Ba 8	.00025	.0370	.339 ± .003	1.530	.144	1.95
Ba 9	.00025	.0370	.337 ± .003	1.528	.142	1.92
Ba P10	.001	.0742	.452 ± .003			
			Calcium as Cation			
Ca 23	0.0333	0.428	0.938 ±0.003	1.972	0.586	0.68
Ca 20	.0250	.371	.888 ± .002	1.948	.562	.76
Ca 21	.0200	.332	.850 ± .002	1.929	.543	.82
Ca 22	.0125	.262	.762 ± .002	1.882	.496	.95
Ca 24	.0125	.262	.759 ± .001	1.880	.494	.94
Ca 1	.0100	.235	.723 ± .003	1.859	.473	1.01
Ca 7	.00500	.166	.618 ± .001	1.791	.405	1.22
Ca 11	.00500	.166	.618 ± .001	1.791	.405	1.22
Ca 6	.00333	.135	.558 ± .002	1.747	.361	1.33
Ca 9	.00333	.135	.561 ± .004	1.749	.363	1.34
Ca 12	.00200	.105	.502 ± .001	1.701	.315	1.50
Ca 4	.00200	.105	.501 ± .001	1.700	.314	1.50
Ca 18	.00150	.0908	.466 ± .002	1.668	.282	1.55
Ca 8	.00100	.0742	.425 ± .003	1.628	.242	1.63
Ca 17	.00100	.0742	.423 ± .001	1.626	.240	1.62
Ca 16	.00050	.0520	.361 ± .001	1.558	.172	1.65
Ca 19	.00050	.0520	.362 ± .001	1.559	.173	1.66
Ca 14	.00025	.0370	.323 ± .002	1.509	.123	1.66
Ca 15	.00025	.0370	.320 ± .002	1.505	.119	1.61
Ca 13	thio-bromo-acetate .00667 / .0033	.178	.636 ± .005	1.803	.417	1.17
			$a = b$			
			Magnesium as Cation			
Mg 18	0.0333	0.428	0.883 ±0.002	1.946	0.560	0.65
Mg 3	.0250	.371	.827 ± .003	1.918	.532	.72
Mg 19	.0200	.332	.801 ± .004	1.904	.518	.78
Mg 20	.0125	.262	.720 ± .001	1.857	.471	.90
Mg 7	.0100	.235	.690 ± .003	1.839	.453	.96
Mg 1	.0050	.166	.576 ± .002	1.760	.374	1.12
Mg 11	.0050	.166	.589 ± .003	1.770	.384	1.16

TABLE I (*Concluded*)

No.	C $a = b$	$\sqrt{\mu}$	k	log k (characteristic negative)	log k/k_0	$\frac{\log k/k_0}{2\sqrt{\mu}}$
Mg 2	0.00333	0.135	0.531 ± 0.002	1.725	0.339	1.25
Mg 12	.00333	.135	.537 ± .002	1.723	.337	1.25
Mg 10	.00200	.105	.485 ± .001	1.686	.300	1.43
Mg 14	.00200	.105	.484 ± .001	1 685	.299	1.42
Mg 6	.00150	.0908	.450 ± .002	1.653	.267	1.47
Mg 5	.00100	.0742	.408 ± .001	1.611	.225	1.52
Mg 13	.00050	.0520	.355 ± .002	1.550	.164	1.58
Mg 15	.00050	.0520	.348 ± .002	1.542	.156	1.50
Mg 16	.00025	.0370	.309 ± .001	1.490	.104	1.41
Mg 17	.00025	.0370	.312 ± .001	1.494	.108	1.46

TABLE II

EFFECT OF ADDED SALTS UPON THE VELOCITY OF THE SODIUM THIOSULFATE–SODIUM BROMOACETATE REACTION

No.	Concn., mole/liter of reacting ions $a = b$	Mole of added salt per liter	$\sqrt{\mu}$	k	log k	log k/k_0	$\frac{\log k/k_0}{2\sqrt{\mu}}$
				Added salt $LaCl_3$			
La 1	0.001	0.00343	0.157	2.85±0.01	0.455	1.069	3.4
La 2	.001	.00572	.196	3.05± .03	.484	1.098	2.8
La 3	.0005	.00172	.111	2.71± .02	.433	1.047	4.7
La 4	.0005	.001372	.101	2.55± .02	.406	1.020	5.1
La 5	.0005	.001022	.0902	2.26± .05	.354	0.968	5.4
La 6	.0005	.000695	.0785	1.91± .02	.281	0.895	5.7
				$MgSO_4$			
Mg 21	.005	.002125	.242	.823± .002	$\bar{1}$.915	...	..
				$MgCl_2$			
Mg 22	.005	.0425	.394	.899± .004	$\bar{1}$.954	...	..
				NaCl			
Na C	.004	3.0 NaCl	1.735	1.55± .02	0.190	.80	0.23
Na D	.004	3.0 NaCl 0.05 $MgCl_2$	1.779	1.50± .03	0.176	.79	0.22
				Saturated Carbon Dioxide			
Na E	.01	P_H = 4.8	0.200	0.645	...	...	..

Compare Na E with Na 3 of Table I.

and five others which showed large deviations from the smooth curve when plotted were rejected.

The results in Table II were obtained by adding salts with trivalent cations to a dilute reaction mixture of the sodium salts. While this method does not permit measurements at very low ionic strengths it shows the profound catalytic effect of trivalent cations upon this reaction.

The theoretical meaning of the results given in the last two columns of Tables I and II will be discussed in detail in another section. Otherwise the headings of the columns are self-explanatory.

VII. Discussion of Results

By plotting the logarithm of the observed velocity constant k against the square root of the ionic strength, equation (4) demands that a straight line be approached having a slope equal to the product of the valences of the reacting ions, namely, $Z_A \cdot Z_B$. The intercept on the ordinate when the ionic strength equals zero corresponds to the value of k_0, the specific reaction velocity constant, which is free from the disturbing concentration influences of interionic attraction provided the experimental data in finite concentrations obey equation (4) with sufficient precision to render the extrapolation trustworthy. A number of investigators have demonstrated the general validity of equation (4) but examples in which it fails are not lacking.[20,3]

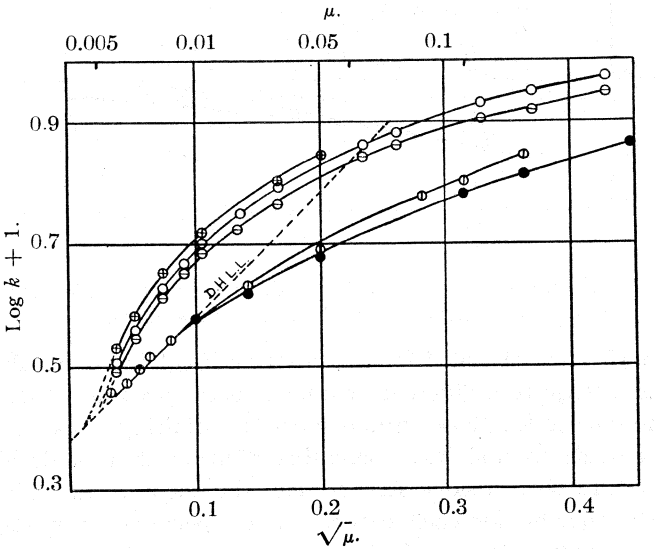


Fig. 1.—⊕, Barium; ○, calcium; ⊖, magnesium; ⊕, potassium; ●, sodium salts.

Our experimental results are shown graphically in Figs. 1 and 2 to test the validity of equation (4). The curve for the univalent potassium ion coincides with the limiting slope ($Z_A Z_B = 2.0$) for values of the square root of the ionic strength less than 0.03. In other words, the limiting law holds for the reaction in the presence of the univalent potassium ion in agreement with the conclusion reached by La Mer[9] for the reaction in the presence of the sodium ion. The new results for the sodium and potassium ion are also identical within the experimental error for values of $\sqrt{\mu}$ less than 0.1 as shown by Fig. 1. This agreement of the experimen-

[20] Conant and Peterson, THIS JOURNAL, **52**, 1220 (1930). See page 1227. See Ref. 3 for reaction of β-bromopropionate ion and thiosulfate ion in highly dilute solutions.

tal results with the Debye–Hückel limiting law in the presence of these univalent cations is in accord with the results of the solubility studies, no appreciable discrepancy having been found for trivalent ions in the presence of univalent ions of opposite sign.

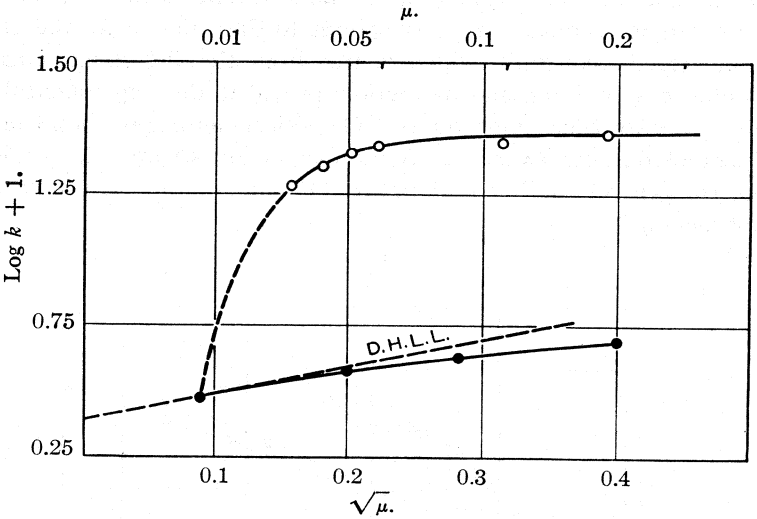


Fig. 2.—Dots, sodium salts; circles, lanthanum chloride added to lowest concentration of sodium salts of reactants.

The kinetic data obtained for this reaction involving a trivalent critical complex are of quite a different character in the presence of divalent cations. The curves for those cations cross the limiting slope at relatively high concentrations and with increasing dilution show a decided downward curvature with a slope steeper than the theoretical. The data are consistently specific for each cation. This specificity persists down to the lowest concentration studied, namely, $\sqrt{\mu} = 0.037$ or $0.00025\ M$ for each reacting ion.

The form of these curves can be interpreted by the solubility studies of La Mer and Mason[5] and the theoretical contributions of Gronwall, La Mer and Sandved.[21] These authors[5,6,7] have shown that the activity coefficients of high valence ions in the presence of high valence ions of opposite sign are considerably smaller than the values calculated by the Debye–Hückel limiting law. The kinetic factor in the reaction under discussion is of the type f_1f_2/f_3 where f_1 refers to the activity coefficient of the bromoacetate ion; f_2 to the thiosulfate ion and f_3 to the triply charged critical complex X. The effect of a high valence cation in the environment will be to give f_3 a value very much smaller than that calculated by the Debye–Hückel limiting law. The values of f_1 and f_2 will also de-

[21] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

crease somewhat in the presence of a high valence cation but the decrease will not be sufficient to effect the decrease in f_3. The total effect on changing the environment from a univalent to a divalent or trivalent cation will be to increase the value of $f_1 f_2/f_3$. The experimental results agree with this prediction. The velocity constants for the reaction in the presence of divalent cations are always greater than those for the univalent potassium or sodium ion. Since this work was completed a paper by King and Jacobs[22] upon the kinetics of the persulfate–iodide reaction has been published. Their results furnish another excellent example of the validity of equation (4) in the presence of the univalent potassium ion. In the presence of added *magnesium sulfate* there is also evidence of a "hump" type curve in their reaction. Unfortunately, as they point out, their reaction is complicated by the presence of the thiosulfate added to measure the progress of the reaction and consequently does not constitute an unambiguous example of this anomaly. The large "hump" noted with the persulfate additions is very likely due to reaction between thiosulfate and persulfate and should not be confused with the present anomaly since it appears at high concentrations.

Since the value of k_0, the velocity constant for the reaction at infinite dilution, must be the same for all cations, all the curves must extrapolate to the same point. Any extrapolation to a limiting value is always burdened with some degree of uncertainty. A linear extrapolation with the aid of a theory based on reasonable postulates and in agreement with the data at finite concentrations involves the least possible uncertainty. We have accordingly evaluated k_0 by a linear extrapolation of the data for the reaction in the presence of the potassium ion in accordance with the limiting slope. The selection of the potassium data is justified by the disappearance of the specific effects of the sodium and potassium ions as demanded by the Debye–Hückel limiting law and by the agreement of the linear portion of the curve with the theoretical value of the limiting slope. This extrapolation gives $\log k_0 = \bar{1}.386$ or $k_0 = 0.243$. Extrapolation of the previous[9] results for this reaction in the presence of the sodium ion gives $\log k_0 = \bar{1}.385$, or $k_0 = 0.243$.

Since the curves for calcium, barium and magnesium must extrapolate to the same value of $\log k_0$ as those of the univalent cations, a point of inflection must occur in the curves for the divalent cations if the limiting slope is reached at extreme dilution. The existence of such a point of inflection is in harmony with the requirements of the Gronwall, La Mer and Sandved[21] extension of the Debye–Hückel theory and with recent experimental data on the behavior of the activity coefficients of cadmium sulfate and of zinc sulfate in high dilution.[23,24]

[22] King and Jacobs, THIS JOURNAL, **53**, 2704 (1931).

[23] La Mer and Parks, *ibid.*, **53**, 2040 (1931).

[24] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

A plot of the results with lanthanum chloride added to the reaction mixture (method *b*) is given in Fig. 2. These results demonstrate the profound catalytic effect produced by changing from a divalent to a trivalent cation. Since lanthanum chloride was added to the sodium salts of the reactants, the curve for lanthanum must join the sodium curve at a point corresponding to the concentration of the sodium salts alone. There will be, therefore, an abrupt change of slope at this point just as in the solubility studies where a foreign neutral salt is added to a solute to increase the solubility. This abrupt change in slope will always occur in the kinetic case when method (*b*) is used. With method (*a*) (only one cation and no foreign anions present) the curve will be smooth and pass through a point of inflection.

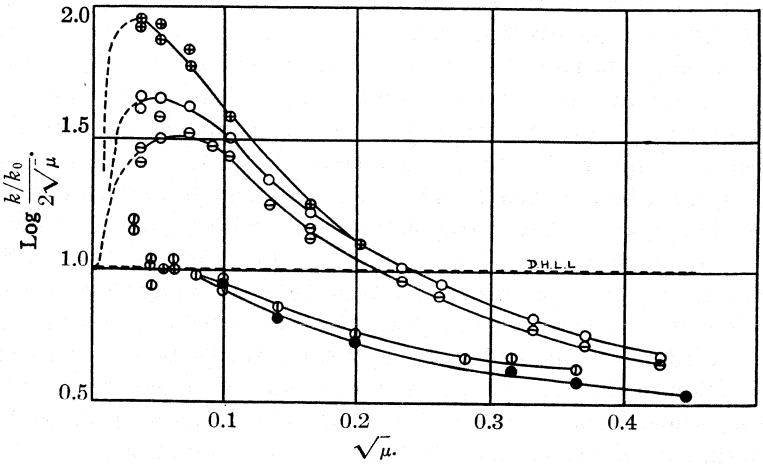


Fig. 3.—⊕, Ba^{++}; ○, Ca^{++}; ⊖, Mg^{++}; ⊕, K^{+}; ●, Na^{+}.

The kinetics of the reaction $2[Co(NH_3)_5Br]^{++} + Hg^{++} \rightleftarrows [X]^{++++} \longrightarrow 2\ [Co(NH_3)_5H_2O]^{+++} + HgBr_2$ involving a tetravalent positive ion as the critical complex were studied by Brönsted and Livingston[4] for the purpose of testing the obedience of the kinetic factor to the limiting law. Although precise activity coefficients have never been obtained for tetravalent ions, nevertheless there is reason to surmise from the freezing point data on $K_4Fe(CN)_6$ and from the e. m. f. data on the ferro–ferricyanide electrode[25] that deviations from the limiting law should persist down to the lowest concentrations studied by Brönsted and Livingston. An examination of their most consistent series (Fig. 5, no added salt) actually yields a limiting *experimental slope of 7 to 8 instead of the theoretical value of 4.* This series also exhibits the same curvature we have shown in Fig. 1 for the divalent cations.

[25] La Mer and Sandved, THIS JOURNAL, **50**, 2656 (1928).

Brönsted and Livingston avoid this conclusion by ignoring their data at the lowest concentrations. Instead they[26] pass a straight line of theoretical slope through the data at intermediate concentrations. The present investigation shows this to be an unwarranted procedure, particularly for reactions between ions of the same sign. Our interpretation would involve a considerable displacement in the extrapolated value of k_0 employed by these authors.

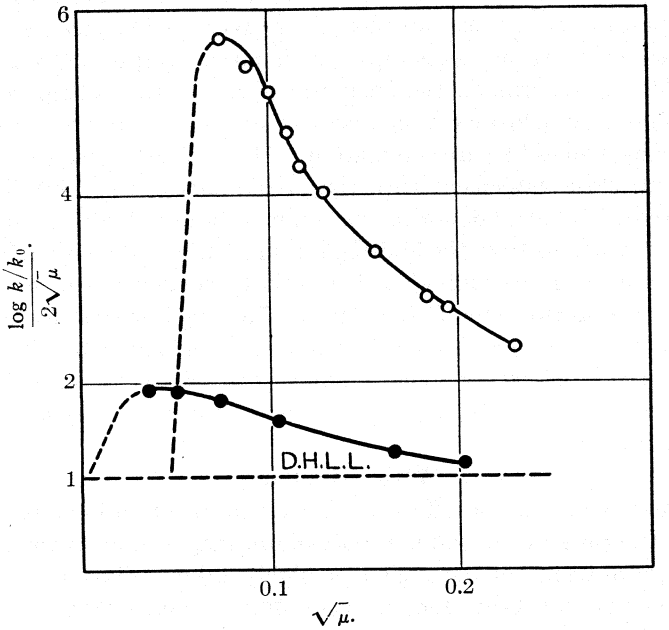


Fig. 4.—○, La^{+++}; ●, Ba^{++}.

From equation (4) it is evident that $\log(k/k_0)/Z_A Z_B \sqrt{\mu}$ is the ratio between the experimental value of the kinetic activity coefficient factor and the ideal limiting value. The values of $\log(k/k_0)/2\sqrt{\mu}$ are given in Tables I and II and plotted in Fig. 3. This plot furnishes a more severe test of the experimental precision in the dilute region and shows the changes in slope as a function of the $\sqrt{\mu}$. The curves for sodium and potassium give a horizontal line (value equal to unity) agreeing within experimental error with the limiting law up to $\sqrt{\mu} = 0.030$. At higher concentrations the ratio decreases. With barium, calcium and magnesium the curve does not approach the limiting value at the lowest concentrations studied. At the higher concentrations the value of $\log(k/k_0)/2\sqrt{\mu}$ is less than unity as in the univalent case. The ratio increases with dilution until it be-

[26] Livingston, *J. Chem. Education*, **7**, 2887 (1930), where a part of the data is replotted.

comes from 40 to 90% greater than the limiting value. The effect is still more pronounced with the lanthanum ion, Fig. 4. At $\sqrt{\mu} = 0.196$ the ratio is over 100% greater than the limiting value and at $\sqrt{\mu} = 0.90$ it has increased to 5.4.

No attempt has been made to treat the kinetic results quantitatively by use of the mathematical expressions for the higher terms of the Poisson–Boltzmann equation as developed for the unsymmetrical case by La Mer, Gronwall, and Greiff.[8] To avoid the introduction of more than one arbitrary parameter the assumption of an average ion size for the three salt types involved is necessary. Such an assumption does not seem justifiable. Furthermore, the structure of the critical complex is so uncertain that any arbitrary assignment of an ion size in the present state of knowledge would be pure speculation. However, the forms of the curves are in such close agreement with the predictions of the solubility studies that there can be little doubt of the common origin of the anomaly. The observed deviations from the limiting law may, therefore, be safely ascribed more to failure of the individual ion activity coefficients in high valence mixtures to conform to the Debye–Hückel limiting law than to an incorrect form of the kinetic activity coefficient correction given by the Brönsted rate equation.[2] However some modifications will very likely be needed to account for orientation,[3] viscosity and non-thermodynamic factors of kinetic influence.

VIII. Summary

The kinetics of the thiosulfate–bromoacetate reaction have been studied at 25° in the presence of sodium, potassium, magnesium, calcium, barium and lanthanum ions in the region of highly dilute solution.

The velocity constants for the thiosulfate–bromoacetate reaction are reproducible in an atmosphere of nitrogen at a concentration of 0.00025 *M* and show no drift with time.

The experimental results for the reaction in the presence of the univalent sodium and potassium ions agree with the theoretical equation developed on the basis of the Debye–Hückel limiting law.

In the presence of the divalent cations deviations of 40 to 80% from the limiting equation were observed while in the presence of the trivalent lanthanum ion a deviation of 440% is found at $\sqrt{\mu} = 0.09$.

A plot of log k against $\sqrt{\mu}$ for the results in the presence of high valence cations exhibits the characteristic types of curves predicted from solubility data for similar valence types and by the La Mer, Gronwall and Greiff extension of the Debye–Hückel theory to unsymmetric valence types, a result which verifies Brönsted's theory of ionic catalysis, but necessarily limits the applicability of the Debye–Hückel limiting law as an extrapolation equation for reactions between ions of the same sign.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

THE SOLUBILITY OF THALLOUS CHLORIDE IN THE PRESENCE OF EDESTIN NITRATE[1]

BY CRAWFORD F. FAILEY

RECEIVED MARCH 2, 1932 PUBLISHED JUNE 6, 1932

One may well begin a discussion of the interaction of salts and proteins in solution by recalling the fact that thermodynamic reasoning cannot decide from measurements of ion activities and concentrations whether there is combination between salt and protein, or whether a decreased activity is due to interionic attraction. We shall set $\gamma = a/m$, where a stands for activity and m for molality, without making any assumption as to how changes in a are brought about. Some particular hypothesis may, however, appear more probable in the light of other physical theories or by analogy with simpler systems.

It will be shown later that edestin changes the mean activity coefficient of thallous chloride

$$\gamma_{\pm} = \sqrt{\frac{a_{Tl^+} a_{Cl^-}}{m^2}} = \sqrt{\gamma_{Tl^+} \gamma_{Cl^-}}$$

by about the same amount as an equal edestin concentration changes γ_{Cl^-}. From this we may conclude that γ_{Tl^+} is affected by the addition of edestin equally with γ_{Cl^-}. An equal binding of Cl^- and Tl^+ in spite of considerable hydrogen ion changes seems unlikely. In opposition to the above may be cited the findings of Northrop and Kunitz,[2] who observed no influence of gelatin on the activity of Li^+, Na^+, K^+, NO_3^- or $SO_4^=$ although these ions should be sensitive to changes in ion atmosphere or dielectric constant if the chloride activity variations be due to these factors.

Experimental

The thallous chloride in this work was the same preparation used by the author in a previous investigation,[3] from which paper values for the solubility in 0.025 molal nitric acid and 0.050 molal nitric acid are taken. The edestin, extracted from hemp seed with 10% sodium chloride, was recrystallized five times from 10% sodium chloride by diluting with three volumes of water at 50° and allowing to cool, then recrystallized twice from 7.5% potassium nitrate by the same method. It was washed free from nitrate by suspending five times in water. Experiments with sodium chloride had shown that this would reduce the salt content to a point where its contribution to the ionic strength could be neglected. The preparation was chloride free.

[1] This work was aided by a grant from The Chemical Foundation.

[2] Northrop and Kunitz, *J. Gen. Physiol.*, **11**, 481 (1928).

[3] Failey, THIS JOURNAL, **54**, 576 (1932).

Determinations of the solubility at 25.00 ± 0.01° were carried out as described in reference 3 except for the method of analysis. The following procedure gave maximum errors of 0.3% on protein solutions of known chloride content. To weighed samples of approximately 100 g. a 50% excess of silver nitrate was added, then 100 ml. of concentrated chloride-free nitric acid. The flasks were digested for twenty-four hours on the steam-bath with the addition of a few drops of caprylic alcohol to prevent foaming. After cooling the silver chloride was washed thoroughly by decantation and weighed in Gooch crucibles with porous porcelain bottoms. Thallous chloride was shown by analysis to be the solid phase in the most concentrated protein solution.

Discussion

The results are tabulated in Table I where the first column indicates grams of edestin per 1000 g. of water; the second, molality of nitric acid; the third, thallous chloride solubility in moles per 1000 g. of water; the fourth, $-\log \gamma_{\pm}$; and the fifth, $\gamma_{\pm}$.

The activity coefficients were obtained by means of the equation $-\log \gamma_{\pm} = \log (1/m_{\pm}^{\circ}) - \log (1/m_{\pm})$ on the assumption that $\log (1/m_{\pm}^{\circ}) = 1.8630$.[4]

TABLE I

Edestin, g.	HNO_3	$S \times 10^5$	$-\text{Log } \gamma_{\pm}$	$\gamma_{\pm}$
0	0.025	1734	0.102	0.791
4.5	.025	1763	.109	.778
13.4	.025	1802	.119	.761
13.8	.025	1827	.125	.733
30.1	.025	1924	.148	.710
34.7	.025	1948	.153	.703
48.8	.025	2043	.173	.691
0	.050	1821	.123	.753
5.2	.050	1842	.128	.745
10.1	.050	1861	.133	.736
24.2	.050	1953	.154	.702
28.1	.050	1971	.158	.695
45.9	.050	2131	.192	.643

Figure 1 is a plot of Table I with $-\log \gamma_{\pm}$ as ordinate and g. of edestin per 1000 g. of water as abscissa. It may be seen that the points for each acid concentration fall approximately on a straight line. Roughly we may set $-\Delta\log \gamma_{\pm}/g = 1.5 \times 10^{-3}$ where g is grams of edestin per 1000 g. of water. The addition of 10.7 g. of edestin has the same effect on $\gamma_{\pm}$ TlCl as 0.1 mole = 7.5 g. of glycine.[3]

Pauli and Stenzinger[5] have measured the solubility of calcium sulfate in protein solutions. Values of $-\Delta\log \gamma_{\pm}/g$ calculated from their data are shown in Table II.

[4] "International Critical Tables," Vol. VII, p. 319.

[5] Pauli and Stenzinger, *Biochem. Z.*, **205**, 71 (1929).

TABLE II

Protein	Salt or ion	$\frac{-\Delta \log \gamma_{\pm}}{g} \times 10^3$	Reference
Edestin	TiCl	1.5	This paper
Serum albumin	$CaSO_4$	1.5	5
Pseudoglobulin	$CaSO_4$	3.9	5
Hemoglobin	$CaSO_4$	4.6	5
Edestin	Cl^-	1.7	6
Gelatin	Cl^-	0.9	6
Gelatin	Cl^-	1.3	2

The e. m. f. measurements of Hitchcock[6] gave results with which the above may be compared. Hitchcock stated that his experiments agree with the assumption that in 0.1 molal hydrochloric acid 1 g. of edestin

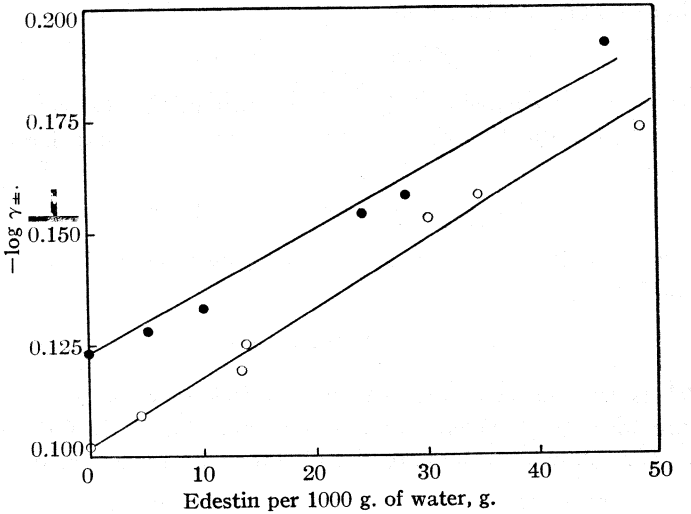


Fig. 1.—○, edestin + HNO_3, $M/40$; ●, edestin + HNO_3, $M/20$.

combines with a maximum of 3.9×10^{-4} mole of Cl^- and 1 g. of gelatin combines with 2.0×10^{-4} mole of Cl^-. This would make a_{Cl^-} and also γ_{Cl^-} a linear function of g. For small changes in γ_{Cl^-} it would be true that $\log \gamma_{Cl^-}$ is also linear. Then for edestin we may set

$$\frac{-\Delta \log \gamma_{Cl^-}}{g} = \frac{\log 0.1 - \log (0.1 - 3.9 \times 10^{-4} g)}{g} = 1.7 \times 10^{-3}$$

For gelatin the value is 0.9×10^{-3}.

Northrop and Kunitz[2] concluded from measurements of membrane equilibria that gelatin may bind approximately 3×10^{-4} mole of Cl^- in $CuCl_2$, per g. of protein. Then $-\Delta \log \gamma_{Cl^-}/g = 1.3 \times 10^{-3}$.

The data of Stadie and Sunderman[7] on the freezing point of solutions

[6] Hitchcock, *J. Gen. Physiol.*, **14**, 99 (1930); *ibid.*, **15**, 125 (1931).

[7] Stadie and Sunderman, *J. Biol. Chem.*, **91**, 227 (1931).

of hemoglobin to which sodium hydroxide has been added offer an opportunity for calculating changes in γ_{Na^+} if one makes the necessary assumption that the authors have been able to "correct for ΔHb." This assumption postulates that in the four term Duhem equation

$$d \ln a_1 = -\frac{m_2}{55.51} d \ln \gamma_2 m_2 - \frac{m_3}{55.51} d \ln \gamma_3 m_3 - \frac{m_4}{55.51} d \ln \gamma_4 m_4$$

where the subscript 1 refers to H_2O, 2 to Na^+, 3 to OH^- and 4 to Hb, the m_3 term is negligible and the m_4 term is unaffected by changes in γ_4. The authors find on adding sodium hydroxide to Hb and also on diluting a solution of NaHb of given Na^+/Hb^- ratio that the observed freezing point depression ascribed to Na^+ is equal to 0.75 the theoretical within the limits of error, or $\varphi_{Na} = 0.75$. On the assumptions made as to a_{Hb} and a_{OH} the Duhem equation reduces to

$$-d \ln a_1 = \frac{m_2}{55.51} d \ln \gamma_2 m_2$$

Following the treatment of Lewis and Randall,[8] observing that $j = 1 - \varphi_{Na^+} = 0.25$ and that $dj = 0$, we have for these small freezing point depressions

$$d \ln \frac{a_2}{m_2} = -j \, d \ln m_2 = -0.25 \, d \ln m_2$$

or, changing to the base 10 and integrating between $m = 0.01$ and any given molality

$$\log \frac{\gamma_2}{\gamma_2^{\#}} = -0.25 (\log m_2 - \log 0.01)$$

where $\gamma_2^{\#}$ is the value of the activity coefficient when $m_2 = 0.01$. If we assume $\gamma_2^{\#} = 0.90$, which is an average value for $\gamma_{\pm}$ in 0.01 molal salt solutions, the following values are obtained for Na^+ in the presence of Hb^-.

TABLE III

m_2	$\gamma_2/\gamma_2^{\#}$	γ^2
0.01	1.00	0.900
.02	.841	.757
.03	.760	.684
.05	.669	.602
.08	.593	.535
.10	.558	.502

TABLE IV

C	γ_{Cl^-}	γ_{Na^+}
0.0125	0.86	0.87
.0128	.89	.87
.0178	.80	.78
.0361	.62	.66
.0404	.65	.64
.0405	.59	.64

These may be compared with the results of Adair[9] on solutions of edestin chloride. The first column given salt concentration; the second, Adair's values for γ_{Cl^-}; and the third, γ_{Na^+} interpolated from Table III.

Tables III and IV are plotted in Fig. 2 together with values of $\gamma_{\pm}$ in sodium chloride solution for comparison.[10] The calculations show that

[8] Lewis and Randall, "Thermodynamics," 1923, p. 285.

[9] Adair, *Proc. Roy. Soc.* (London), **A120**, 573 (1928).

[10] Taylor, "Treatise on Physical Chemistry," 1931, Vol. I, p. 772.

with a constant φ_{Na^+} there is associated a considerable change in γ_{Na^+} as the molality is varied. Figure 2 indicates the agreement between the work of Adair and that of Stadie and Sunderman, although the latter authors, assuming that constant φ implied constant γ, found contradictions. It may finally be pointed out that Adair's values would give a much greater $-\Delta\log \gamma_{Cl^-}/g$ than any shown in Table II.

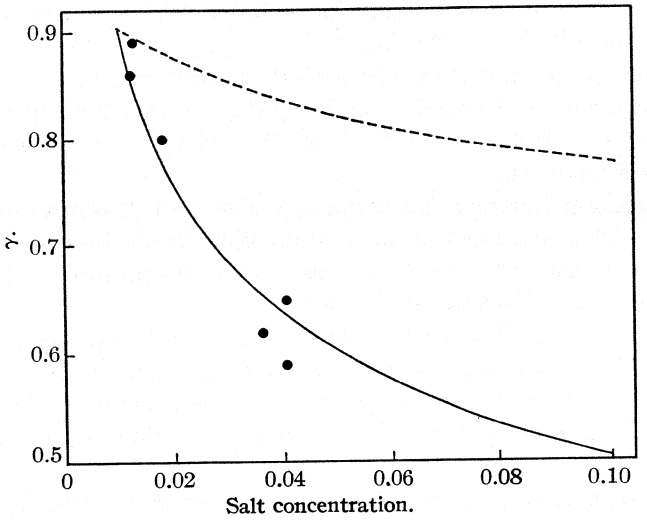


Fig. 2.—The points are Adair's values for γ_{Cl^-} in edestin chloride. The full line represents γ_{Na^+} in the presence of hemoglobin assuming $\varphi_{Na^+} = 0.75$ and that $\gamma_{Na^+} = 0.90$ when $c = 0.01$. For comparison the broken line gives $\gamma_{\pm}$ in aqueous sodium chloride solutions.

Summary

The solubility of thallous chloride in solutions of edestin nitrate has been determined. The negative logarithm of the activity coefficient of thallous chloride is approximately a linear function of grams of edestin per 1000 g. of water. Some existing data on the activity of salts in the presence of protein have been compared.

New York City

[CONTRIBUTION FROM THE TOWNE SCIENTIFIC SCHOOL OF THE UNIVERSITY OF PENNSYLVANIA]

THE COMPOSITION OF MAGNESIUM OXYCHLORIDE

BY H. S. LUKENS

RECEIVED MARCH 3, 1932 PUBLISHED JUNE 6, 1932

The composition of magnesium oxychloride has been the subject of a number of reported investigations.[1]

The more recent investigations indicate uncertainty as to the existence of definite compounds of MgO and $MgCl_2$. It was the purpose of this investigation to endeavor to establish the existence or absence of such definite combinations.

The Reaction between Magnesium Oxide and Magnesium Chloride Solutions.—The solubility of magnesium oxide in solutions of magnesium chloride with the subsequent formation of a precipitate in the filtered solutions was first reported by G. André.[2]

The product of this reaction was subsequently investigated by W. Feitknecht,[1] who showed that the products resulting from the interaction of magnesium oxide and magnesium chloride bear a definite relation to the source of the magnesium oxide, *i. e.*, whether obtained by the ignition of the carbonate or oxalate.

The present investigation had, as an initial objective, the investigation of the reaction between magnesium chloride solutions and magnesium oxide obtained by the ignition of magnesium hydroxide.

Experimental

For the purpose of these experiments, magnesium oxide of the following analysis was used:

[1] Sorel, *Compt. rend.*, **65**, 102 (1867); Bender, *Ber.*, **3**, 932 (1871); *Liebig's Ann.*, **159**, 341 (1871); Davis, *Chem. News*, **25**, 258 (1872); Krause, *Liebig's Ann.*, **165**, 38 (1873); André, *Compt. rend.*, **94**, 444 (1882); Andre, *Ann. chim. phys.*, [VI] **3**, 79 (1884); Moldenhauer, *Z. anorg. Chem.*, **51**, 369 (1906); Hof, *Chem.-Ztg.*, **32**, 993 (1908); *ibid.*, **33**, 693 (1909); Kallauner, *ibid.*, **33**, 871 (1909); Robinson and Waggaman, *J. Phys. Chem.*, **13**, 673 (1909); Krieger, *Chem.-Ztg.*, **34**, 246 (1910); Lahrman, *Tonind.-Ztg.*, **35**, 265 (1911); Kallauner, *Chem.-Ztg.*, **37**, 1045 (1913); Krieger, *ibid.*, **37**, 1274 (1913); Kallauner, *ibid.*, **37**, 1275 (1913); Edwards, *Concrete Cement Age*, [1] **4**, 184 (1912); Ralston, Pike and Dushak, *Bur. Mines Bull.*, 236 (1925); Maeda, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, [5] **76**, 141–154 (1926); Maeda and Yamane, *ibid.*, [4] **50**, 85 (1926); Maeda, *ibid.*, [5] **73**, 95 (1926); Feitknecht, *Helv. Chim. Acta*, **9**, 1018 (1926); **10**, 140 (1927); **13**, 1380 (1930); Maeda, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, [5] **75**, 133 (1926); Maeda and Yamane, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **7**, 340 (1928); Kurnakov, Zhemchuzhnuii, and Agieva, *Zhur. Prikiadnoi Khim.*, **2**, 651 (1929).

[2] André, *Compt. rend.*, **94**, 444 (1882).

	Maximum Impurities, %		
Water-soluble substances	0.7500	Nitrates (N_2O_5)	0.0064
Insoluble in HCl	.0000	Barium (Ba)	.0200
Sulfates (SO_3)	.0250	Calcium (Ca)	.0200
Chlorides (Cl)	.0100	Iron (Fe)	.0250
Carbonates	Trace	Other heavy metals	.0000

The material was digested with an excess of distilled water for twenty-four hours at a temperature of 100°. It was then dried on a steam-bath and heated to constant weight at a temperature of 110°. A sample ignited to constant weight at 1000° showed a loss of 30.86% as contrasted with a calcd. loss of 30.88%.

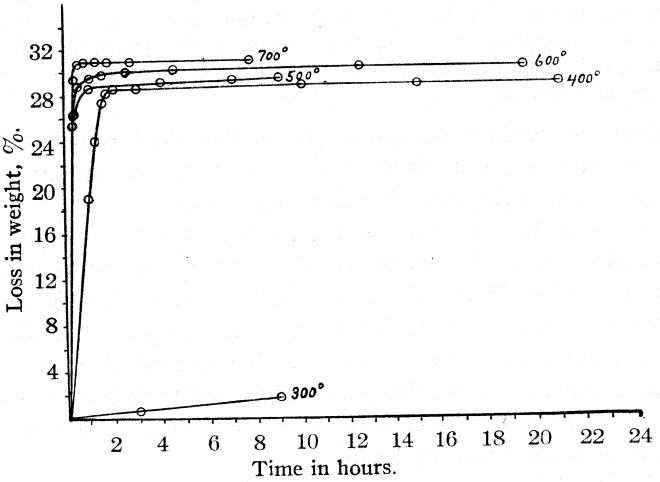


Fig. 1.—Effect of temperature on magnesium hydroxide; $Mg(OH)_2 \rightarrow MgO + H_2O$—loss = 30.88 %. Reaction at 800°, complete in 30 min.; reaction at 900°, complete in 15 min.; reaction at 1000°, complete in 10 min.

Lacking data regarding the rate at which magnesium hydroxide loses water at various temperatures, this subject was investigated with the results indicated in the graphs, Fig. 1. The rate of loss was determined by heating 7- to 8-g. samples in platinum in an electrically heated muffle at the desired temperature for ten-minute (or longer) intervals. The crucible and contents were then cooled in a phosphorus pentoxide desiccator and weighed. The oxide produced by low temperature calcination was extremely hygroscopic and the greatest care was required to secure reproducible results. The oxide produced by calcination at 900 and 1000° was quite inert and could be exposed to the atmosphere of the balance case without detectable change over a period of an hour.

The technique adopted for the determination of the rate of solution of magnesium oxide in magnesium chloride solutions was as follows.

A weighed amount of magnesium oxide was triturated in a mortar with a 25-cc. portion of magnesium chloride solution. Mortar, pestle, magnesium oxide and magnesium chloride solution were previously brought to the working temperature selected. The solution was decanted into a test-tube of 125 cc. capacity. The heavy particles which remained, after decanting the liquid carrying considerable solid material in suspension, were ground with the liquid remaining until all the large particles were reduced to a uniform suspension. A second portion of magnesium chloride solution was then added and the same operations repeated. On decanting a third 25-cc. portion from the mortar, all solid particles appeared to have been removed. A fourth 25-cc. portion of magnesium chloride solution served to assure the complete removal of all solid particles and brought the volume of magnesium chloride solution to a total of 100 cc. The stoppered tube and contents were placed in a constant temperature bath and turned end over end at a velocity of fifteen turns per minute throughout the duration of the experiment. At intervals, 10-cc. portions of the contents of the tube were withdrawn and the amount of magnesium oxide in solution determined by filtering and titrating a 5-cc. portion of the filtrate with $N/5$ hydrochloric acid, using phenolphthalein as an indicator.

The above described procedure proved to yield reproducible results, whereas no success was attained in attempting to prepare samples of magnesium oxide of like particle size by screening.

The graphs in Fig. 2 represent results obtained by following the foregoing procedure at a temperature of 30°. The graphs for magnesium oxide prepared at 500 and 600° fall regularly between those for 400 and 700° and are therefore omitted. At higher temperatures, up to 40°, the curves fall in the same relation to one another with the time decreased; at lower temperatures, down to 10°, the time is increased with decrease in temperature. The figures in brackets represent the time and temperature of calcination of magnesium hydroxide.

From the graphs, it is apparent that there is a definite relationship between the thermal treatment of the magnesium oxide and the rate of solution as well as the amount of oxide dissolved. The rate of precipitation of the new compound, once saturation is attained, is substantially the same in all cases.

An increase in the ratio of the amount of oxide to the amount of magnesium chloride solution decreases the time required to attain saturation and the amount of oxide dissolved increases [Graph 2 g., twenty-one hours, 400°]. A decrease in the ratio of oxide to solution retards the rate of formation of the insoluble precipitate to a marked degree [Graph 0.5 g., twenty-one hours, 400°].

In all cases the concentration of magnesium oxide in the solutions decreased as more and more precipitate was formed, finally approaching the solubility of magnesium hydroxide in the solution under investigation.

The following procedure was developed for the preparation of the precipitate. A sample of oxide of known thermal history was triturated in a mortar with magnesium chloride solution, as previously described, and the suspension, contained in a stoppered tube, was then agitated in a constant temperature bath. After the lapse of sufficient time to effect saturation of the solution with oxide, as indicated by the graph correspond-

ing to that oxide, the concentration of the magnesium chloride solution used, and the temperature, the excess oxide was removed from the solution by filtration. The clear filtrate was placed in a clean flask and returned to the constant temperature bath. Here it was allowed to remain until sufficient precipitate collected to provide a sample for analysis. The precipitate was then removed by filtration, dried rapidly by suction, and washed with 75- to 100-cc. portions of absolute alcohol prepared as recommended by G. Frederick Smith.[3] The washing with alcohol was conducted by removing the

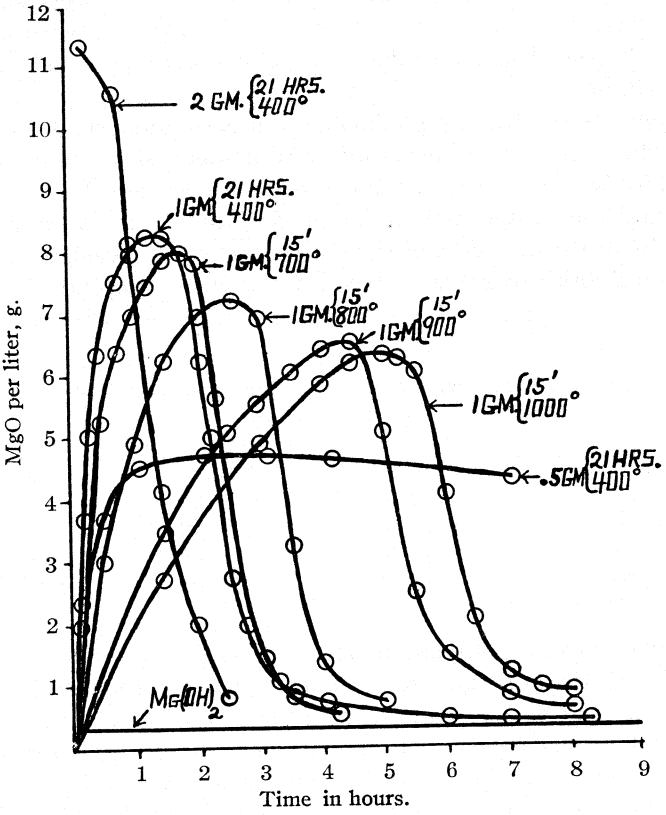


Fig. 2.—Solubility of magnesium oxide in magnesium chloride solution of sp. gr. 1.179; temperature 30°.

gelatinous precipitate to a flask and stirring with a rod while covered with a small portion of alcohol. More alcohol was then added and the mixture shaken violently until a uniform suspension of precipitate in alcohol was attained. The alcohol was then removed by filtration, with suction, and the operation repeated with additional portions of alcohol until successive portions of filtrate, when tested, indicated a low constant chlorine content. This was found to correspond to 0.213 g. of soluble material per liter. From six to eight portions of alcohol were required to complete the washing. The material was then heated at a temperature of 100° to constant weight. As the material was hygroscopic, it was introduced into weighing bottles while warm and samples for

[3] Smith, *Ind. Eng. Chem., Anal. Ed.*, **1**, 2, 72 (1929).

analysis were measured by determining the weight of bottle and contents before and after pouring out samples.

The precipitates, while forming, appeared to consist of minute crystals. On removal from the solutions they were observed to have all of the characteristics of a gel. On washing with alcohol the precipitates lost their gel-like properties and became decidedly crystalline. This change was accompanied by a marked decrease in volume. It was observed, however, that if a washed and dried precipitate were again treated with magnesium chloride solution, it again attained the gel-like character and regained its former volume.

Many efforts to obtain reproducible results on analysis of samples prepared in this way were unsuccessful, until it was realized that there was a relationship between the time the precipitate remained in the chloride solution and the composition of the precipitate. A few results are tabulated to illustrate the effect of time of contact of the precipitates with the magnesium chloride solutions from which they were precipitated. The chlorine content is assumed to be present in the form of magnesium chloride.

TABLE I

EFFECT OF TIME OF CONTACT WITH MAGNESIUM CHLORIDE SOLUTIONS ON COMPOSITION OF PRECIPITATE

MgO, 1 g., 30 hours, 400°. $MgCl_2$, 100 cc. Sp. gr. 1.179. Temp., 25°

Time precipitate remained in solution	Composition of precipitate MgO, %	$MgCl_2$, %	H_2O, %
1 hour	44.61	20.34	35.05
10 hours	44.34	21.38	34.28
24 hours	38.84	25.08	36.08
10 days	35.96	26.84	37.20
9 months	36.51	27.07	36.42

With such evidence, strongly indicative that the ratio of $MgCl_2$ to MgO increased with time of exposure of the precipitate to the solution in which it formed, an effort was made to determine whether the precipitate, as formed, was homogeneous. Two portions of a precipitate were collected. One portion represented that which formed at first and which was removed from solution within one hour after precipitation started. The second portion was the precipitate which formed between one hour after and four hours after precipitation started. After removal of the second portion, a further small amount of precipitate formed but this was discarded. On analysis of the two portions of precipitate, the following results were obtained.

TABLE II

COMPOSITION OF INITIAL AND FINAL PORTIONS OF PRECIPITATE

MgO, 1 g., 30 hours, 400°. $MgCl_2$, 100 cc. Sp. gr., 1.179. Temp., 25°

Period of time after precipitation started during which sample was formed	Composition of precipitate MgO, %	$MgCl_2$, %	H_2O, %	Ratio MgO: $MgCl_2$
0 ⟶ 1 hour	42.42	20.09	37.49	4.97 : 1
1 hour ⟶ 4 hours	42.51	20.07	37.42	5.00 : 1

From the above and similar data it was concluded that the precipitate, as formed, was uniform in composition.

To determine definitely whether a precipitate changed in composition on further contact with the solution in which precipitation took place, the following experiment was conducted. Five grams of magnesium oxide (30 hours, 400°) was treated with 250 cc. of magnesium chloride solution of sp. gr. 1.179 at a temperature of 25°. The precipitate formed after filtering remained in contact with the solution at constant temperature for a period of ten days. On analysis the precipitate was found to have the following composition: MgO, 42.35%; $MgCl_2$, 20.85%; H_2O, 36.80%; ratio of MgO:$MgCl_2$, 4.79:1. Further data relating to such changes are presented later.

To determine whether the precipitates differed in composition when prepared from samples of magnesium oxide of different thermal history, experiments were conducted from which the following results were obtained.

TABLE III

COMPOSITION OF INITIAL PRECIPITATES OBTAINED FROM MAGNESIUM OXIDE SAMPLES OF DIFFERENT THERMAL HISTORY

MgO, 1 g. $MgCl_2$, 100 cc. Sp. gr., 1.179. Temp., 25°

Type of MgO	Composition of precipitates: MgO, %	$MgCl_2$, %	H_2O, %	Ratio MgO : $MgCl_2$
21 hours, 400°	44.62	20.39	34.99	5.12 : 1.00
36 hours, 500°	42.56	20.08	37.36	5.01 : 1.00
30 min., 800°	42.72	19.93	37.35	5.06 : 1.00
10 min., 1000°	44.68	20.28	35.04	5.20 : 1.00

It is evident that within the range covered, the mole ratio of magnesium oxide to magnesium chloride approaches 5:1, irrespective of the thermal treatment of the oxide from which the precipitates are prepared.

Temperature was found to have a marked effect on the velocity of the reaction. At 20° only a slight precipitate formed within twenty-four hours; in forty-eight hours precipitation was complete. Raising the temperature from 25 to 30° increased the rate of solution of oxide approximately 50%. Change in temperature was found to have no detectable effect on the ratio of magnesium oxide to magnesium chloride in the precipitates as is illustrated in Table IV.

TABLE IV

EFFECT OF TEMPERATURE ON COMPOSITION OF INITIAL PRECIPITATES

MgO, 1 g., 30 hours, 400°. $MgCl_2$, 100 cc. Sp. gr., 1.179

Temperature during formation, °C.	Composition of precipitates: MgO, %	$MgCl_2$, %	H_2O, %	Ratio MgO:$MgCl_2$
20	44.35	21.38	34.27	4.89 : 1.00
25	42.41	20.11	37.48	4.98 : 1.00
30	42.72	20.05	37.23	5.03 : 1.00

To determine whether the composition of the precipitate was influenced by the specific gravity of the magnesium chloride solutions employed, precipitates were made at 25° using magnesium oxide prepared at 400°, and magnesium chloride solutions of sp. gr. 1.124, 1.142, 1.148, 1.151, 1.160, 1.179 and 1.265. The results of the analysis of these precipitates are shown in the graphs, Fig. 3.

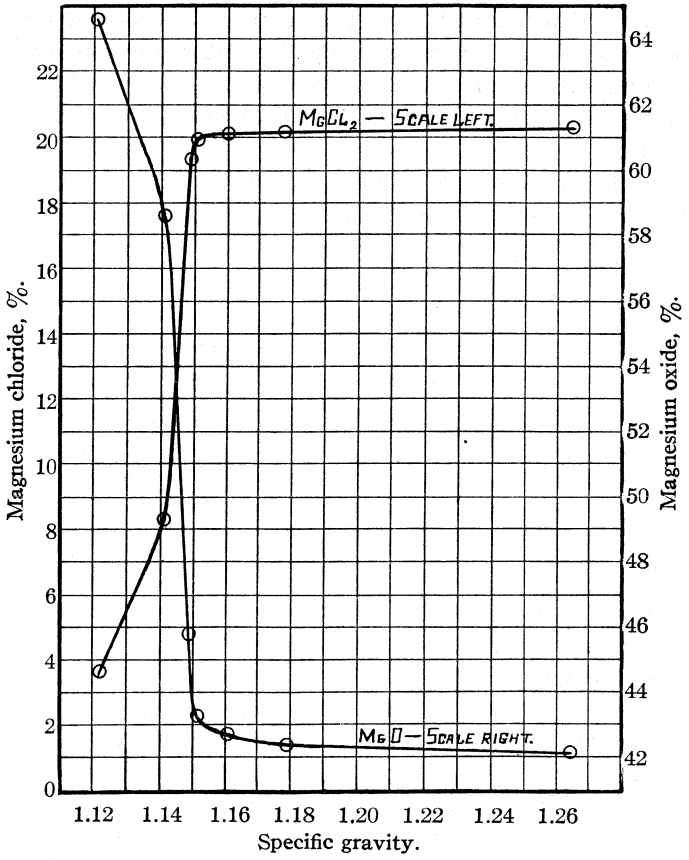


Fig. 3.—Composition of initial precipitates with change in specific gravity of magnesium chloride solutions.

The precipitates were removed from solution within five to six hours after the first contact of the oxide with the solutions. The precipitate produced in solution of sp. gr. 1.151 appeared to be more crystalline than those produced at higher concentrations. The precipitate formed in solution of sp. gr. 1.124 was decidedly flocculent.

It is obvious from the graphs that in solutions of sp. gr. below 1.16 the magnesium oxide content of the precipitates increases while the magnesium

chloride content decreases correspondingly. Such findings may be explained on the assumption that in solutions of low specific gravity, magnesium oxide combines with water to form magnesium hydroxide rather than a compound with magnesium chloride. From solutions of sp. gr. 1.16 up to sp. gr. 1.265 the initial precipitates consist of a combination of magnesium oxide, magnesium chloride and water in which the ratio of magnesium oxide to magnesium chloride is 5 to 1.

Robinson and Waggaman[4] describe a compound formulated $3MgO \cdot MgCl_2 \cdot 10H_2O$. As this compound was formed after equilibrium was attained between the interacting constituents, it seemed of interest to investigate further the action of magnesium chloride solutions on the compounds just described. A precipitate corresponding to the 5 to 1 ratio was prepared. One-half was used for analysis, the other portion was covered with 50 cc. of magnesium chloride solution, sp. gr. 1.265, and agitated in a stoppered tube at 25° for ninety hours. The results of the analysis of the precipitates before and after treatment are given in Table V.

TABLE V

CHANGE IN COMPOSITION OF INITIAL PRECIPITATE WHEN AGITATED WITH MAGNESIUM CHLORIDE SOLUTION

	Composition of precipitates			Ratio
Precipitate	MgO, %	$MgCl_2$, %	H_2O, %	MgO : $MgCl_2$: H_2O
Initial precipitate	42.56	20.08	37.36	5.01 : 1.00 : 9.84
Precipitate after treatment with magnesium chloride for 90 hours	34.86	26.38	38.76	3.48 : 1.00 : 7.76

A precipitate was prepared and allowed to remain in contact with the solution for a period of ten days at 25°. Four samples of 2 g. each were placed in flasks, covered with 100 cc. of magnesium chloride solution, sp. gr. 1.325, the flasks stoppered and allowed to remain undisturbed in a constant temperature bath at 25° until removed for analysis. Analyses were made at intervals over two years with results indicated in Table VI.

TABLE VI

CHANGE IN COMPOSITION OF INITIAL PRECIPITATE ON UNDISTURBED CONTACT WITH MAGNESIUM CHLORIDE SOLUTION

	Composition of precipitates			Ratio
Treatment of precipitate	MgO, %	$MgCl_2$, %	H_2O, %	MgO : $MgCl_2$: H_2O
Original precipitate	42.35	20.86	36.79	4.79 : 1.00 : 9.32
After 5 months	38.30	24.99	36.71	3.62 : 1.00 : 7.76
After 11 months	36.55	27.25	36.20	3.16 : 1.00 : 7.02
After 18 months	36.45	27.39	36.16	3.14 : 1.00 : 6.98
After 24 months	36.49	27.11	36.40	3.17 : 1.00 : 7.09

The ratio of magnesium oxide to magnesium chloride described by Robinson and Waggaman is confirmed. The water content differs,

[4] Robinson and Waggaman, *J. Phys. Chem.*, **13**, 673 (1909).

probably due to the difference in the methods used in the preparation of samples for analysis.

Up to the present it has not been possible to devise any method for determining the water content of the precipitates. The gel-like appearance indicates that the amount of water is greater than indicated by the analyses. The water is obviously loosely held, for even protracted washing with absolute alcohol tends to reduce the water content as is evident from the data in Table VII.

TABLE VII

LOSS OF WATER BY $5MgO \cdot MgCl_2 \cdot xH_2O$ ON WASHING WITH ALCOHOL

Number of times washed with anhydrous alcohol	Composition of precipitate			Ratio
	MgO, %	$MgCl_2$, %	H_2O, %	MgO : $MgCl_2$: H_2O
7 completed within an hour	42.56	20.08	37.36	5.01 : 1.00 : 9.84
10 over a period of 4 days	51.27	24.14	24.59	5.06 : 1.00 : 5.43

When exposed to the atmosphere of a phosphorus pentoxide desiccator, both compounds lose water steadily. The compounds were not in equilibrium with the desiccator atmosphere even after 111 hours at a pressure of 5 mm. On heating, both compounds will, in time, come to constant weight at any given temperature up to 200°. After heating for thirty-five hours at 200°, the 5 to 1 compound lost 17.16% of its weight after drying over phosphorus pentoxide at 5 mm. for 111 hours; the 3 to 1 compound lost 24.67%.

Summary

Magnesium oxide is shown to dissolve in magnesium chloride solutions with the subsequent precipitation of a compound in which the ratio of magnesium oxide to magnesium chloride is 5 to 1, loosely combined with an unknown amount of water.

The velocity of the reaction is determined principally by the thermal treatment of the magnesium oxide and by the temperature at which the reaction takes place.

The compound initially precipitated in solutions of magnesium chloride of concentrations above sp. gr. 1.16 may be formulated $5MgO \cdot MgCl_2 \cdot xH_2O$.

The compound $5MgO \cdot MgCl_2 \cdot xH_2O$ on continued treatment with magnesium chloride solution of sp. gr. above 1.16 is transposed to a new compound which may be formulated $3MgO \cdot MgCl_2 \cdot yH_2O$.

No satisfactory method has been devised for determining the water content of the compounds as formed in solution.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PHOTOCHEMICAL TECHNIQUE. I. A SIMPLE CAPILLARY MERCURY VAPOR LAMP

BY FARRINGTON DANIELS AND LAWRENCE J. HEIDT

RECEIVED DECEMBER 8, 1931 PUBLISHED JUNE 6, 1932

This lamp[1] was designed to meet the demand for an intense source of ultraviolet light for photochemical investigations and particularly for illuminating the slit of a monochromator. Mercury lamps and other sources of ultraviolet light have been reviewed.[2,3] Forbes and his coworkers[4,5] have developed an effective capillary mercury vapor lamp and have studied carefully its characteristics. The lamp described here is less permanent and it must be water cooled, but it is simpler and cheaper. One can afford to run it at a great overload, thus giving a higher intensity.

Description

The simplified lamp, shown in Fig. 1, is made of quartz tubing[6] with an inside diameter of 1 to 2 mm. and a wall 0.7 to 1 mm. in thickness. Tubes of larger diameter may be used. A tube about 12 cm. long is provided with two bulbs, A and B, blown out in the gas–oxygen flame with a space of 5 to 30 mm. between them when operated on d. c. line voltages of 50 to 600 volts, respectively. The bulbs are blown as thin as is consistent with mechanical strength. Their function is to keep the arc localized between A and B. They prevent the arc from extending farther, because the thin walls are cooler and because the larger diameter reduces the current density. The more completely the arc is thus localized the steadier is the lamp. Tungsten electrodes, 0.5 mm. smaller in diameter than the containing tube, are preferable, but nickel or iron (hay wire) may be used.

The upper, positive electrode, E, is set with de Khotinsky cement (shellac and pine tar) flowed into the warmed tube as shown by the cross hatching. The lamp is filled by placing the open end under purified mercury, evacuating and then releasing the vacuum. The lamp is then inverted and the electrode D is sealed in with cement. Silver chloride or other high melting, sealing cements used with bulbs in the earlier models are unnecessary if a rapid stream of cold water is employed. The uppermost

[1] Preliminary descriptions have been given in THIS JOURNAL, **52**, 2151 (1930), and in Daniels, Mathews and Williams "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1929, p. 423.

[2] Ellis and Wells, "The Chemical Action of Ultraviolet Light," Chemical Catalog Co., New York, 1925.

[3] Forbes, *J. Phys. Chem.*, **32**, 485 (1928).

[4] Harrison and Forbes, *J. Opt. Soc. Am.*, **10**, 1 (1925); **11**, 99 (1925); THIS JOURNAL, **47**, 2449 (1925).

[5] Leighton and Forbes, *J. Phys. Chem.*, **30**, 1628 (1926).

[6] Quartz tubing may be purchased from the Hanovia Chemical and Manufacturing Co. of Newark, N. J., from the General Electric Co., Schenectady, N. Y., from the Thermal Syndicate, Brooklyn, N. Y., or from The Quartz Products Manufacturing Co., 69 Tichenor St., Newark, N. J. The cost of tubing for a lamp is less than a dollar.

bulb, C, serves as the expansion chamber into which the mercury is driven when the arc is struck and the space between A and B is filled with incandescent mercury vapor. The size of this bulb and the level of the mercury determine the expansion volume. The ratio of the arc volume to this expansion volume determines the pressure under which the lamp operates. A small expansion volume gives a high pressure and a correspondingly high resistance. When 550 volts are available, the volume can be small, leading to pressures of 2 to 5 atmospheres and giving high-voltage, low-amperage lamps.

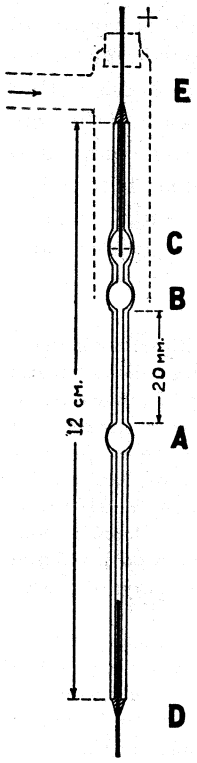


Fig. 1.—Capillary mercury vapor lamp of quartz. Inside diameter, 2 mm. Wall thickness, 0.7 to 1.0 mm.

The protruding electrodes of the lamp are connected with rubber-insulated wires and the bare connections are then insulated by covering with de Khotinsky cement. The wires are connected with a direct current dynamo through an adjustable resistance. A 22-ohm, 5-ampere resistance is sufficient for use on a 110-volt circuit but on a 550-volt circuit several additional resistances are necessary.[7] The resistance of the lamp varies from nearly zero before the arc is struck, to 20 to 500 ohms when operating depending on the expansion volume and on other factors.

Cooling with a large, rapid stream of cold water is absolutely necessary. Without it the seals and the quartz itself are melted. Hard water may be used if the stream is sufficiently rapid; otherwise, the outside of the lamp becomes hot enough to form a deposit.

To start the lamp the mercury is shaken down, the circuit is closed and the mercury thread in the capillary is then separated by playing on it a small Bunsen flame. The instant the arc strikes, water is turned on. The lamps have been started, also, with a small electric heating coil wound around the capillary just above the bulb A.

The protruding end of the upper electrode passes through a rubber stopper which fits into a T-tube of glass 1 cm. in diameter, extending to the bulb B. The tube is shown by dotted lines in Fig. 1. In this way an encircling stream of water is directed down around the lamp to a waste pipe. Best results are obtained by mounting the lamp in a copper tank provided with a quartz window and drain and overflow tubes, 3 cm. or more in diameter. A brass frame soldered to the tank and a similar frame screwed against it hold the quartz window in place with rubber gaskets. The tank is emptied with the drain, and after the lamp is started the tank is allowed to fill, thus completely immersing the lamp.

Caution.—There is danger from a lamp bursting although the stream of water and particularly the tank mounting minimizes this danger. Special care is necessary to avoid ultraviolet burns.

The lamps operate well on 110 volts and 3 to 5 amperes. A 550-volt source permits greater intensity. If the lamps fail to start properly it may be necessary to (a) increase the voltage, (b) decrease the mercury level, thus giving a greater expansion chamber, a lower pressure and consequently a lower resistance and higher current, or (c) change the diameter of the capillary. If the current increases seriously while the lamp is operating one may suspect a leak at the seals. More effective cooling is then necessary. An inexpensive ammeter should be included in the circuit.

[7] "Glow" resistances, for radiant heaters, which screw into an electric light socket, are convenient and cheap.

Tests

Each lamp has its own characteristics but in general the intensity of radiation, E_λ, of a particular wave length is nearly proportional to the wattage, W, of the lamp. The formula $E_\lambda = aW$, is a rough approximation to the average behavior between 500 and 1500 watts. When E_λ is determined as ergs per second falling on a sq. mm. of a thermopile after passing through a large monochromator and W is the product of the amperage and the voltage drop across the lamp, the constant a has the following values: 1 for 265 and 280 mμ; 5 for 302 mμ; 7 for 313 mμ; 2 for 334 mμ; from 12 to 20 for 365 mμ; from 4 to 8 for 404 mμ; and from 6 to 12 for 436 mμ. The short ultraviolet lines give about the same intensity per watt regardless of the voltage, but the 404 and 436 mμ lines are more intense at high voltages. The larger values of a correspond roughly to 500 volts and the smaller values to 100 volts. The distribution of energy will be shown more fully in Fig. 3 of the following article. The lines below 265 mμ are weak and there is extensive reversal of the line at 253.6 mμ.

Plotting amperes through the arc as ordinates against voltage across the arc as abscissas, the curve passes through a maximum. However, plotting resistance across the arc as ordinates against voltage the curve is linear.

Aging varies. Perhaps twenty-four hours of operation is a common life. When operating below 500 watts, a lamp may last much longer. After heavy usage, a white deposit forms on the inside of the lamp which shows, under the microscope, a distorted honeycomb structure. For the internal 0.05 mm., however, these minute cracks are fused together, showing that the effective temperature of the arc is above the melting point of quartz (1700°). The outside of the tube 0.7 to 1 mm. away from the arc is at about 20° and the cracks may be due to this enormous temperature gradient, or possibly to crystallization. The white region of cracks does not cause a large reduction in intensity but a few cracks spread out and eventually one of them causes the lamp to break. Lamps with thick walls break much sooner than those with thin walls.

The efficiency of the lamps was tested also with 100 cc. of a solution, 0.8 molar in oxalic acid and 0.05 molar in uranyl sulfate, placed in a hollow, cylindrical, quartz cell completely surrounding the lamp. Using a lamp at 570 volts and 2.7 amperes, 6.16 g. of oxalic acid was decomposed in eight minutes, corresponding to 0.77 g. per minute and to 0.24 mole per kilowatt hour. Taking the quantum efficiency of this reaction as 0.6 molecule per quantum[8] the photochemical action consumed 0.4 einstein (1 einstein = 6.06×10^{23} quanta) per kilowatt hour of energy supplied to the lamp. Similar results were obtained with a stream of solution passing through a concentric, cylindrical cell only 5 cc. in capacity. In experiments with rectangular quartz cells at a distance of about 10 cm. these

[8] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

capillary lamps gave over one hundred times as much photochemical action as a commercial lamp.

The chief reason for the high intensity (per sq. mm. of lamp surface) is the high concentration of energy. The volume of the arc in the capillary lamp is approximately 0.05 cc. as against 20 cc. in a commercial lamp. Although the volume of a commercial lamp is 400 times as great, the total input of energy is less. The dimensions of the capillary lamp are such that a much greater fraction of the radiation emitted by the lamp can be brought to the slit of a monochromator or passed into a reaction cell of ordinary dimensions.

The authors are pleased to acknowledge the help contributed by Mr. Glenn Damon and Mr. Harrison Holmes to the development of the lamp described here.

Summary

An inexpensive quartz mercury vapor lamp of high intensity has been described and tested.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PHOTOCHEMICAL TECHNIQUE. II. CONSTRUCTION AND TESTS OF A QUARTZ MONOCHROMATOR[1]

BY LAWRENCE J. HEIDT AND FARRINGTON DANIELS

RECEIVED MARCH 10, 1932 PUBLISHED JUNE 6, 1932

Monochromatic radiation of measured intensity is necessary for the quantitative study of photochemical reactions. Separation of the different wave lengths by refraction in a monochromator offers the most effective method for obtaining this radiation but the energy flux available at any one wave length is extremely low on account of losses due to reflection, absorption, slit dimensions, etc. To minimize this handicap a more intense source of light was developed.[2] Further efforts to increase the radiation intensity by using a monochromator of large dimensions and favorable optical conditions are described in the present communication.

The subject of monochromators and of photochemical apparatus has been reviewed in detail by G. S. Forbes.[3] The dimensions and material of the prism and lenses used in the present investigation are approximately those described by Marshall and Knudson.[4] The purpose of

[1] Complete details of the dimensions and calculations may be obtained from the Ph.D. Thesis (June, 1930) of the first author, which is on file in the Library of the University of Wisconsin.

[2] Daniels and Heidt, THIS JOURNAL, **54**, 2381 (1932).

[3] Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

[4] Marshall and Knudson, *ibid.*, **52**, 2304 (1930).

this article, then, is to describe and to present tests for an efficient method of mounting an optical system of fused quartz used as a monochromator. The mechanism described automatically keeps the prism at minimum deviation and in the center of the field, and provides automatic focusing. Previously this has been accomplished by means of compound prism arrangements or mirrors. Included in the tests is a study of the photodecomposition of uranyl oxalate made prior to the publication of the classic paper of Leighton and Forbes.[5]

Description of Monochromator

Side and top views of the monochromator and accessories are shown in Figs. 1 and 2. A is a 60° fused quartz prism 12 cm. on a side and 14 cm. high. B and B′

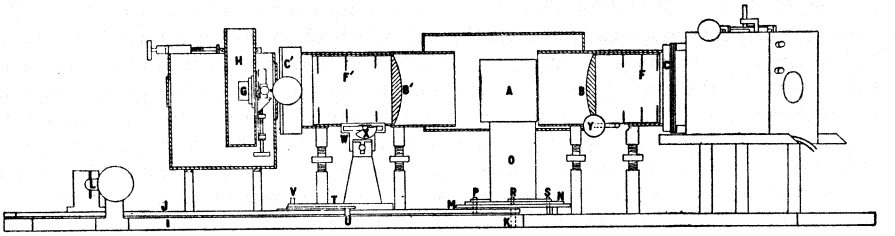


Fig. 1.—Monochromator, side view.

are fused quartz lenses 15.25 cm. in diameter, each with a focal length of 35 cm. for λ795 mμ. C and C′ are slits shown in detail in Fig. 2a. The pupil C is curved to make the exit beam rectangular. D is the source of radiation previously described.[2] Fine

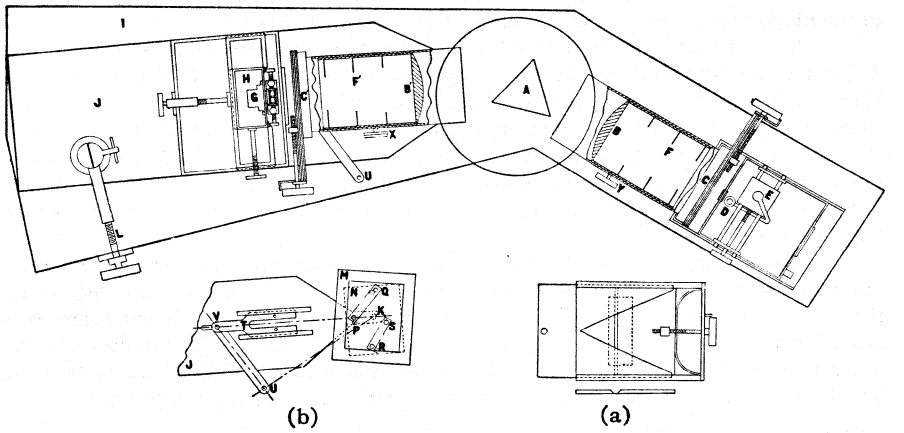


Fig. 2.—Monochromator, top view.

adjustments placing the source on the principal axis of B are made by a screw attached to E. F and F′ are graduated elliptical diaphragms three of which are placed in each of the collimator and telescope tubes to diminish stray light. The latter are brass tubes

[5] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

telescoping freely without play by means of the rack and pinion arrangements X and Y.[6] G is a thermopile mounted flush against a slit built into a vertical track in which G slides in a submarine H. Directly in front of G is mounted on H an adjustable support for reaction vessels. Fine adjustments of H, G and the support can be made in three dimensions by means of appropriate screws, not all of which are shown in the cuts. The submarine and the cells are immersed in distilled water thermostated to 0.1°. A double-convex quartz lens (not shown) 5 cm. in diameter with a focal length of 5 cm. for λ 795 mμ placed between C′ and the reaction vessel renders the light parallel when passing through the latter to the thermopile. I is the weathered and planed cast-iron base 200 cm. long. Leveling is accomplished by means of screw supports in the base, not shown. J is a steel plate on which the telescope is mounted. This plate, mounted on brass tracks, is pivoted about the intersection, K, of the principal axes of the collimator and telescope. Gross and fine adjustments of J are made by the screw, L, equipped with a split nut.

M, N, O, P, Q, R and S in Figs. 1, 2 and 2b comprise a mechanism such that (a) the prism is turned through half the angle through which the telescope is turned to keep it at the angle of minimum deviation, and (b) the center of the prism is displaced along the bisector of the angle between the axes of the collimator and telescope to keep it in the center of the field. This displacement (b) is 8.4 mm. in passing from $n_{795\ m\mu}$, 1.4534 to $n_{185\ m\mu}$, 1.5746 for fused quartz. N is a brass plate which slides on a horizontal brass plate M; a pin in N, over K, engages a slot in M. M and N have slots for the passage of pins, P and S. The position of N for a short wave length is shown by its dotted outline in Fig. 2b. O is the prism table. Its center, the center of the fixed pin in N which engages the slot in M, and a point on the perpendicular bisector of the base of the prism, A, lie on a straight line. P is a pin fixed on the principal axis of the telescope lens to J. Q is a pin fixed to N and joined to P by means of a rigid bar equipped with fine adjustments for length. R is a similar pin fixed to N and similarly joined to S. S is a pin fixed on the principal axis of the collimator lens to I. P, Q, R and S and the slot in the center of M are placed such that Q, K and R are always on a straight line in the plane of the perpendicular bisector of the base of the prism.

T, U, V, W and X in Figs. 1, 2 and 2b comprise the mechanism for automatic focusing. T is a metal fork which clears the post supports of the telescope. U is a pin fixed in I. V is a pin free to move along the axis of the telescope in a rectangular slot cut in J. The rod connecting U and V has a fine adjustment for length. W is a rack mounted on T. W rides on a cog wheel X. The turning of X actuates another wheel and rack which moves B′ in a corresponding fashion to V. X, which is mounted in a split nut, may be disengaged from the shaft driving B′ thus permitting hand adjustment. Y permits hand adjustment of B.

The whole apparatus is adjusted by hand for some definite wave length (one of the known lines of the mercury lamp); the lenses B and B′ are then set at equal distances in the tubes. The automatic adjustments are then set. Thereafter the monochromator is set for different wave lengths by turning the screws L and Y. The positions for the different wave lengths are marked on a scale under L in the floor, I, of the instrument. The lens B is set by hand at the same relative position as B′, using a depth gage.

Tests of the Monochromator.—Figure 3 is an energy distribution curve[7] of a mercury vapor capillary arc lamp[2] as determined with this monochromator. Any adjustments of the prism or lenses by hand follow-

[6] Internal surfaces are blackened with an alcoholic solution containing lamp black and shellac, which while drying is smoked thoroughly with camphor black.

[7] Compare with data of Harrison and Forbes, *J. Optical Soc. Am.*, **10**, 1 (1925).

ing automatic adjustment to a mercury line always caused a decrease in the energy flux through the exit slit. The upper and lower curves are for slit widths of 0.6 and 0.1 mm., respectively; the height of the slits in both cases was 20 mm. The total energy flux (ordinate) in ergs/sec. (upper curve only) passing through the exit slit was determined by means of a

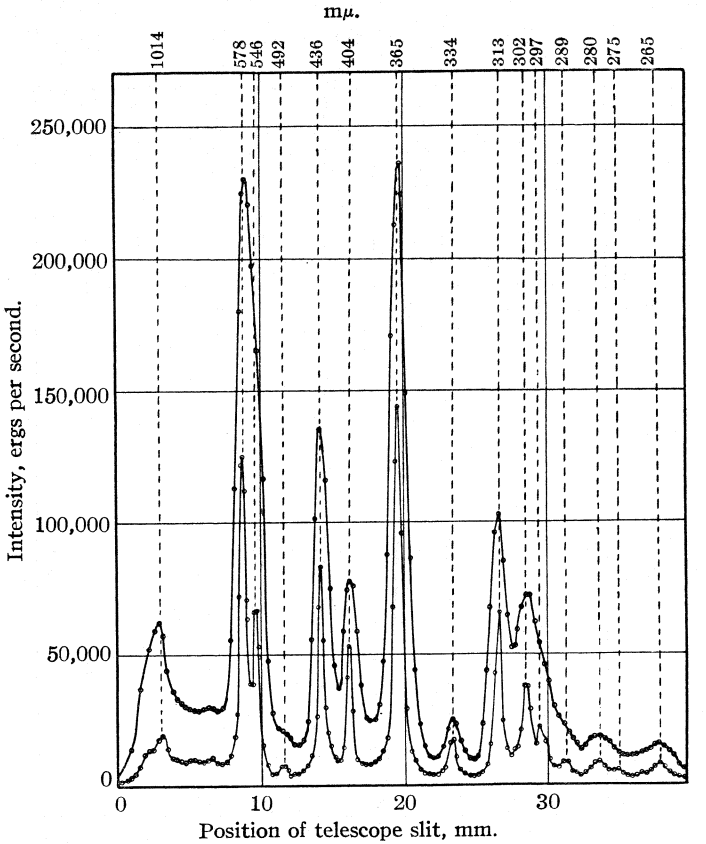


Fig. 3.—Energy distribution: upper curve, 0.6-mm. slits; lower curve, 0.1-mm. slits; capillary lamp, 200 volts, 5.5 amperes, 1100 watts; the scale of ordinates applies only to the upper curve.

large thermopile to be described later. The thermopile–galvanometer circuit and accompanying shunts was calibrated against U. S. Bureau of Standards lamp C44. The abscissa represents clockwise turns of L in terms of the distance between a fixed point on L and its split nut attached to J. The absence of λ 254 mμ due to absorption by the fused quartz should be noted. That this line and shorter wave lengths are present in the source was proved by a spectrogram.

The intensity of radiation of λ 313 mμ was compared under identical

conditions with a commercial monochromator having a prism 3 cm. high. The monochromator described here gave more than ten times as much intensity.

The degree of monochromatism obtainable with this instrument was tested (*a*) qualitatively by spectrophotometry and (*b*) quantitatively by radiometry.

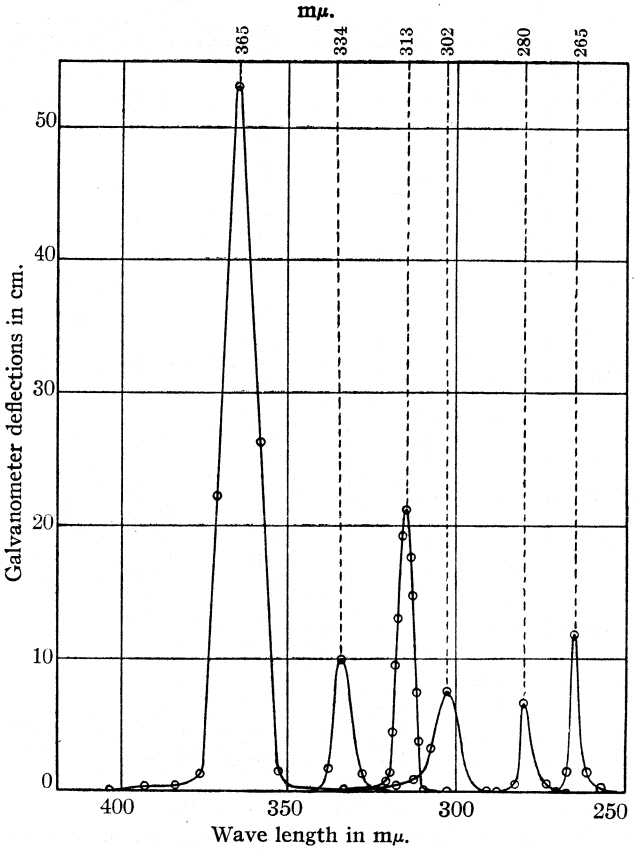


Fig. 4.—Efficiency of the monochromator as determined with a second monochromator.

(*a*) Using a carbon arc as a continuous source, slit widths of 0.6 mm. and the instrument set at λ 420 mμ, a spectrogram of the emerging light showed a blackening which covered 20 mμ (as determined by reference to the 436 and 404 mμ lines of mercury photographed on the same spectrogram) about this wave length.

Using a mercury arc as source and the monochromator under identical conditions, a spectrogram showed complete isolation of 436 or 404 mμ, depending on the setting of the monochromator. Exposures of several

seconds, however, gave spectrograms showing all the prominent lines of mercury. Similar tests applied to a commercial monochromator showed it to be less efficient than this instrument.

(*b*) The energy distribution of light emerging from the large monochromator at given settings for maximum intensity of the wave length in question is shown by the curves in Fig. 4. These curves were determined using the mercury arc[2] as source, slit widths of 0.6 mm. and a second monochromator with thermopile–galvanometer. "Purity" of the light may be obtained by estimating the area (counting squares) under these peaks be-

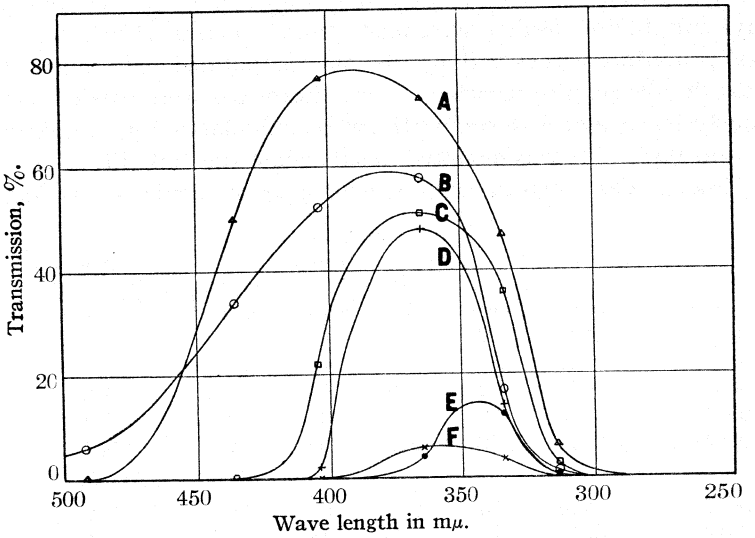


Fig. 5.—Percentage transmission of various glass filters of thicknesses stated: A, blue-purple ultra, 3.91 mm.; B, cobalt glass, 2.61 mm.; C, red-purple ultra, 4.17 mm.; D, red-purple ultra, 5.08 mm.; E, ultraviolet filter IVc, 4.57 mm.; F, ultraviolet glass, 8.91 mm.

tween definite limits. The limits, of course, depend on the energy distribution of the lamp, wave length and the width of the slits of the second monochromator. At 365 and 313 mμ 98% of the total energy recorded on the thermopile of the second monochromator fell between 353 and 375 mμ and between 310 and 320 mμ, respectively. It was gratifying, particularly since the quartz lenses and prism contained many small bubbles and some striations, to find that, although all the mercury lines were recorded on a spectrogram, the intensity of the other lines was less than 1% of the one selected by the first monochromator. Spectrograms of any one of 436, 404, 365, 334, 313 and 302 mμ emerging from the exit slit of the two monochromators in tandem (using slit widths of 0.6 mm.) showed only the wave length in question on exposures as long as ten minutes.

Comparison with Filters.—Purity [method (*b*) used] of light transmitted by certain filters is shown in Fig. 5. With the exception of B these were standard filters purchased from the Corning Glass Works. Comparison with Fig. 4 shows that the monochromator is much more effective than these filters in restricting the light to a narrow range of wave lengths.

The Photodecomposition of Uranyl Oxalate.—The photolysis of oxalic acid at 313 mμ and at room temperature in the presence of uranyl salts affords a more direct test of the efficiency of this monochromator in the study of photochemical reactions. Materials used were of C. P. quality and when purchased as such were not subjected to further purification. Uranyl sulfate and oxalate were made from C. P. uranyl nitrate. Experimental procedure was essentially the same as that of Leighton and Forbes.[5] Several details require mention. Two photolyses were carried out simultaneously by using a two-compartment rectangular cell with quartz plates front and back. It was mounted flush against the exit slit, C′, on a platform (Figs. 1 and 2) which could be moved perpendicular to the axis of the

TABLE I

$[UO_2C_2O_4]$	$[H_2C_2O_4]$	% 313 mμ absorbed	Depth of cell in cm.	Time of photolysis in minutes	Quanta absorbed $\times 10^{-18}$	Molecules $H_2C_2O_4$ decomposed $\times 10^{-18}$	Quantum yield, gross
0.0005	0.0045	72	2.0	60	17.9	9.0	0.51
.0005	.0045	72	2.0	45	11.8	6.6	.56
.0005	.0045	72	2.0	60	8.4	6.2	.74
.0005	.0045	72	2.0	60	10.0	7.4	.75
.0005	.0045	72	2.0	60	12.5	8.1	.64
						Average	.64
.0017	.0330	86	1.0	60	16.0	7.2	.45
.0017	.0330	86	1.0	45	11.2	5.3	.47
.0017	.0330	86	1.0	30	7.7	3.4	.44
						Average	.46
.0017[a]	.0330	86	1.0	45	6.2	3.3	.53
$[UO_2SO_4]$							
.0017	.0330	86	1.0	60	15.1	7.8	.51
.0017	.0330	86	1.0	60	15.8	9.3	.59
.0017	.0330	86	1.0	45	11.0	7.1	.65
.0017	.0330	86	1.0	45	11.0	6.8	.62
.0017	.0330	86	1.0	90	21.8	12.1	.56
.0017	.0330	86	1.0	30	8.1	5.0	.61
						Average	.59
$[UO_2(NO_3)_2]$							
.0017	.0330	86	1.0	30	7.5	3.7	.50
.0017	.0330	86	1.0	60	16.2	10.5	.65
.0017	.0330	86	1.0	90	25.8	14.3	.55
.0017	.0330	86	1.0	45	12.4	6.4	.51
						Average	.53

[a] $MgSO_4$ is 1 Molar.

telescope lens. Solutions in each compartment were photolyzed alternately for ten-minute intervals. Energy flux transmitted by the solution was measured at three-minute intervals by a thermopile, G (a Coblentz twenty junction silver–bismuth thermopile, 20 mm. × 1 mm.), placed directly behind the reaction cell. The maximum change in per cent. absorption by the solution during photolysis was always less than 2%, usually less than 1%.

Results of this part of the investigation are presented in Table I. Concentrations are given in moles per liter. These results show that the anion of the uranyl sensitizer has little effect on the quantum yield—the oxalate, sulfate and nitrate giving nearly the same results. Even the addition of magnesium sulfate in high concentrations has little effect on the gross quantum yield.

Leighton and Forbes[5] report gross quantum yields for 0.01 *m* uranyl sulfate in 0.05 *m* oxalic acid of 0.545, 0.53, 0.57, 0.595 and 0.57, giving an average value of 0.561. The good agreement between the two researches gives confidence not only in the monochromator described here, but in the general reliability of quantitative photochemical measurements.

The authors desire to acknowledge the help given by a du Pont Fellowship held by the first named author during the progress of this work.

They desire also to thank Mr. J. H. Hanson for the careful machine work involved in the building of the monochromator.

Summary

1. A monochromator for the investigation of photochemical reactions in the ultraviolet has been described. An automatic device, not using a reflecting mirror or a compound prism arrangement, keeps the 60° prism at minimum deviation and in the center of the field. Another device keeps the telescope automatically in focus.

2. Radiation of over 100,000 ergs per second from the prominent lines of a capillary mercury vapor lamp are obtainable with this monochromator.

3. "Purity" of monochromatic light obtainable from the monochromator has been tested in several ways, and compared with that of filters. Approximately 98% of the radiation at any wave length setting falls within a range of 10 to 20 mμ.

4. In the presence of uranyl sulfate, 0.59 molecule of oxalic acid is photochemically decomposed for each quantum absorbed at 313 mμ and at 27 ± 2°. This result is in close agreement with that of Leighton and Forbes. Uranyl sulfate, nitrate and oxalate used as sensitizers give practically the same results.

MADISON, WISCONSIN

NOTES

Needle-Shaped Crystals of Sodium Chloride Obtained by Percrystallization

By Henry Tauber and Israel S. Kleiner

In 1917 the observation was made by Kober,[1] that if a collodion container, filled with a saturated ammonium sulfate or a saturated sodium chloride solution, and with the open end closed tightly with a cord, was suspended in the air and fanned in a warm room, crystals of these salts "crystallized on the outside and blew off like snow." He called this phenomenon "percrystallization." To our knowledge no use has been made since that time of this method of crystallization. While working on the purification of enzyme material, we thought that this method would afford a practical way of getting rid of the inorganic diffusible salts and at the same time of concentrating the enzyme. We found that the sodium chloride, which was present in the enzyme-salt mixture, crystallized outside the collodion bag, but instead of the usual cubic habit, the sodium chloride crystallized in beautiful needles about 1 cm. long (see Fig. 1).

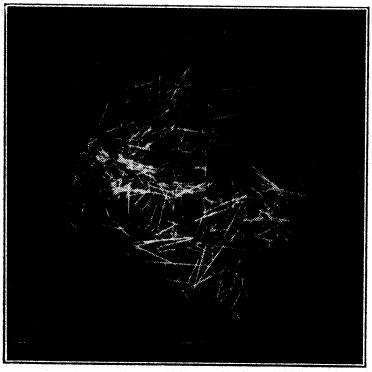


Fig. 1.—Crystals of sodium chloride obtained by percrystallization, natural size.

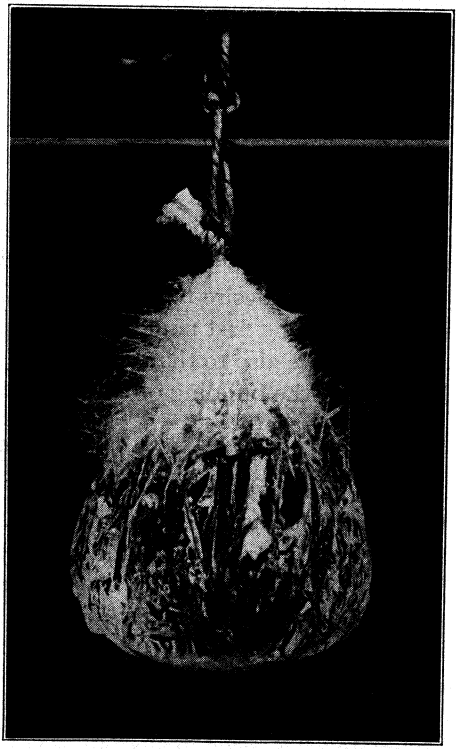


Fig. 2.—Collodion bag with sodium chloride needles forming by percrystallization.

The procedure (without fanning), repeated with C. P. sodium chloride (Baker's), yielded the same needles. One hundred fifty cc. of a half-satu-

[1] Kober, This Journal, **39**, 944 (1917).

rated solution was placed in a 250-cc. collodion bag at 20°. Within one hour the needles (see Fig. 2) crystallized outside on the upper part of the bag, above the level of solution.

Drs. W. J. McCaughey of Ohio State University and J. B. Niederl of New York University examined these crystals and found that they belong to the regular cubic system.

The fact that the crystals mainly develop in one direction seemed to be worthy of note.

We are greatly indebted to Professors W. J. McCaughey and J. B. Niederl for examining the crystals.

CONTRIBUTION FROM THE
DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
NEW YORK HOMEOPATHIC MEDICAL COLLEGE
AND FLOWER HOSPITAL
NEW YORK CITY

RECEIVED FEBRUARY 19, 1932
PUBLISHED JUNE 6, 1932

The Generalized Theory of Acid and Base Catalysis Applied to the Rate of Ionic Reactions

BY ROBERT LIVINGSTON

The rate of the catalytic decomposition of hydrogen peroxide in an acid bromine–bromide solution has been measured both in solutions of hydrobromic acid and in solutions containing sulfuric acid and potassium bromide.[1]

The corrected rate constant, χ in the equation

$$v = \chi(H_2O_2)(H^+)(Br^-)\gamma^2_{HBr}{}^2$$

is about 10% higher for the solutions containing sulfuric acid. While it is not impossible that this difference is due to experimental error,[3] it seems more probable that it is a real effect, probably due to the specific catalytic action of the acid molecule HSO_4^-.[4] Although the generalized theory of acid (and base) catalysis has never been demonstrated for reactions between ions, there is no *a priori* reason why this type of reaction should not occur. On the assumption that HSO_4^- acts similarly to and simultaneously with H_3O^+, the total rate equation would be

$$v = (H_2O_2)(H^+)(Br^-)\left[\chi_{H_3O}\gamma^2_{HBr} + \chi_{HSO_4}\frac{(HSO_4^-)}{(H^+)}\frac{\gamma_{HSO_4^-}\gamma_{Br^-}}{\gamma_x}\right]$$

While this is qualitatively in agreement with the experimental facts, a quantitative test is impossible, owing to uncertainties in the computation

[1] (a) Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048 (1923).

[2] Livingston, *ibid.*, **48**, 53 (1926).

[3] It might be due to "promoter action" or to negative catalysis, caused by a trace of some unknown impurity, or else to a systematic error in the determination of the activity coefficients.

[4] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

of (HSO_4^-) and the impossibility of determining $\gamma_{HSO_4^-}\ \gamma_{Br^-}/\gamma_x$. In sufficiently dilute solutions these quantities might be computed from the Debye–Hückel limiting law; unfortunately, accurate rate measurements would be practically impossible in this region. The occurrence of generalized acid catalysis in this reaction might be tested by using solutions containing small concentrations of potassium bromide and a moderately weak, chemically inert acid in the presence of a high constant concentration of an inert salt, *e. g.*, sodium perchlorate.

Other ionic reactions might be expected to show a similar effect; for example, the oxidation of hydriodic acid by chloric acid,[5] or the basic hydrolysis of the nitrourethan ion.[6]

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED JANUARY 2, 1932
PUBLISHED JUNE 6, 1932

[5] Bray, *J. Phys. Chem.*, **7**, 92 (1903).

[6] Brönsted and Delbanco, *Z. anorg. allgem. Chem.*, **144**, 248 (1925).

The Entropy of Bromine from Spectroscopic Data

BY WELDON G. BROWN*

A recent fine structure analysis of the visible absorption bands of bromine by the writer[1] has provided data from which accurate values of the thermodynamic constants of bromine may be calculated. These calculations involve nothing essentially new, although certain consequences of a rather unique isotope situation become emphasized. In this note the entropy calculated from band spectrum data is to be compared with a less accurate value obtained from experimental measurements of the specific heat.

There are two isotopes of bromine, 78.92 and 80.92, which, according to Aston's measurements,[2] are equally abundant. These give rise to three kinds of molecules, Br_2^{79}, $Br_2^{79,81}$ and Br_2^{81}, in the proportions 1:2:1, respectively. A slight difference in the molecular constants of the Br_2^{79} and Br_2^{81} molecules leads to slightly different entropies, but because of their equal abundance this becomes smoothed out when, in calculations of thermodynamic constants, one uses the data for the $Br_2^{79,81}$ molecule. There is an additional effect due to the lack of symmetry which results in the entropy of $Br_2^{79,81}$ being greater than the entropy of either of the symmetrical species by R ln 2 per mole, or $^1/_2$ R ln 2 per mole of the actual mixture since this species constitutes one-half of ordinary bromine.

The moment of inertia of bromine is sufficiently large and the centrifugal

* National Research Fellow.

[1] Brown, *Phys. Rev.*, **39**, 777 (1932).

[2] Aston, *Proc. Roy. Soc.* (London), **115**, 487 (1927); **132**, 489 (1931).

deformation sufficiently small to make applicable the approximation in summation of the rotational energy terms used by Gibson and Heitler, and by Giauque,[3] in the case of iodine, namely

$$Q_{\text{rot.}} = \sum_i p_i e^{-\epsilon_i/kT} = \frac{4\pi^2 IkT}{h^2} = \frac{T}{2c_2 B}$$

where c_2 is the second radiation constant, and B is the fine structure constant obtainable directly from the spectral data. This expression applies to a symmetrical molecule. The entropy is then obtained by the well-known formula[4]

$$S^\circ = R\left[\ln Q + T\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right]$$

The band spectrum constants for the normal electronic state of $Br_2^{79.81}$ are as follows. The subscripts refer to the zero vibrational state.

$$B_0 = 0.08077 \qquad \omega_0 = 322.2$$
$$\alpha = 0.00027 \qquad \omega_0 x_0 = 1.07$$

In the following table the molal entropies (ideal gas, pressure one atmosphere, at 298.1°K.), calculated as indicated above, are given for each of the three molecular species, together with the entropy of the 1:2:1 mixture exclusive of the entropy of mixing. It is to be noted that the entropy of the mixture, 59.32 E. U., is equal to the entropy of $Br_2^{79,81}$ minus $^1/_2\ R \ln 2$.

	$S_{\text{trans.}}$	+	$S_{\text{vib.}}$	+	$S_{\text{rot.}}$	=	$S^\circ_{298.1}$
$Br_2^{79,79}$	41.07		1.30		16.19		58.56
$Br_2^{79,81}$	41.11		1.31		17.59		60.01
$Br_2^{81,81}$	41.15		1.32		16.23		58.70
1:2:1 mixture	$^1/_4$(58.56)		$^1/_2$(60.01)		$^1/_4$(58.70)		59.32

Comparison with specific heat measurements can be made most conveniently at the melting point temperature, 265.8°K., at which the vapor pressure, according to Henglein,[5] is 44.12 mm. From the band spectrum data we calculate $S_{265.8^\circ}$ (p = 44.1 mm.) = 61.69 E. U., assuming a perfect gas. The specific heat measurements of Suhrmann and v. Lude[6] extend down to 20.5°K., but are few in number and somewhat erratic. From the smoothed points given by them we obtain, for the entropy of solid bromine at its melting point, 25.5 E. U., the uncertainty in which must be of the order 1.0 E. U. The entropy of vaporization at the melting point is 36.6 E. U. if we accept Henglein's value for the heat of vaporization, 9740 cal. The experimental value for the entropy of bromine gas at this temperature and pressure is then 25.5 + 36.6 = 62.1 E. U., in good agreement with the value 61.69 calculated from spectroscopic data.

[3] Giauque, THIS JOURNAL, **53**, 507 (1931).
[4] Giauque, *ibid.*, **52**, 4808 (1930).
[5] Henglein, *Z. Physik*, **11**, 1 (1922).
[6] Suhrmann and v. Lude, *ibid.*, **29**, 71 (1924).

However, the entropy, as calculated above, cannot be used for chemical purposes without reference to the entropy of mixing of isotopes. This entropy of mixing is $^3/_2\ R$ ln 2 per mole, while for the free atoms (or for HBr, for example) it is R ln 2 per mole. If, by convention, the entropy of mixing of the atoms is to be excluded, the value for the entropy which we have calculated must be reduced by $^1/_2\ R$ ln 2. For bromine gas in its standard state this results in the value $S^\circ_{298.1} = 58.63$ E. U. The value is thus the same as if the additional entropy of $Br_2^{79,81}$ resulting from its additional states had been considered as a part of the entropy of mixing of isotopes. This places Br_2 on the same basis as HBr, the entropy of which has been calculated from band spectrum data by Giauque.[7]

The equilibrium constants for the dissociation of bromine at high temperatures, calculated by means of the Gibson and Heitler[8] equation and the band spectrum constants, are in poor agreement with the experimental values of Bodenstein.[9] The discrepancy, for which no explanation is offered, amounts to 0.15 in log K and is constant with temperature. The writer plans a further check on the entropy of bromine through the use of the experimental data for the dissociation of iodine bromide. An analysis of the iodine bromide absorption bands, which will provide the necessary spectroscopic data, is now in progress.

RYERSON PHYSICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED JANUARY 14, 1932
PUBLISHED JUNE 6, 1932

[7] Giauque, THIS JOURNAL, **50**, 2193 (1928).
[8] Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).
[9] Bodenstein, *Z. Elektrochem.*, **22**, 327 (1916).

The Recombination of Hydrogen Atoms

BY GEORGE E. KIMBALL

In a recent paper Steiner[1] has made some very interesting calculations on the rate of recombination of hydrogen atoms by triple collisions with hydrogen atoms and molecules as third bodies. He assumes that the recombination takes place in two steps: (1) the formation of an atom pair, or quasi-molecule, and (2) the stabilization of the energy-rich atom pair by collision with a third body during its lifetime τ. Throughout this work Steiner has overlooked the fact that there is another, equally probable, mechanism for the recombination. This mechanism may also be divided into two steps, but these are now: (1′) collision of a hydrogen atom with a hydrogen molecule, and (2′) collision of this quasi-molecule with a new hydrogen atom to form two hydrogen molecules.

Steiner finds theoretically that the diameter of a hydrogen atom in (1)

[1] Steiner, *Z. physik. Chem.*, **B15**, 249 (1932).

is 2.5–3.5 $\times 10^{-8}$ cm., and that the lifetime τ of the atom pair is 2.5–4.5 $\times 10^{-14}$ sec. By comparison of the theory with experiment he then finds that the effective diameter of H_2 as a stabilizing third body must be 6.7–12.5 $\times 10^{-8}$ cm. By considering the mechanism (1′), (2′) we find that the required diameter of the molecule H_2 is a much more reasonable value.

The rate of process (1′) is given by

$$Z_{AM} = 2\sqrt{2\pi}\, N_L^2 \sigma_1^2 \left(\frac{3RT}{2M}\right)^{1/2} [C_H][C_{H_2}] \qquad (1)$$

and the stationary concentration of the quasi-molecules H_3 is given by

$$[C_{H_3}] = \frac{Z_{AM}\,\bar{\tau}}{N_L} = 2\sqrt{2\pi}\, N_L \sigma_1^2 \left(\frac{3RT}{2M}\right)^{1/2} [C_H][C_{H_2}]\,\bar{\tau} \qquad (2)$$

The symbols used in these equations are those used by Steiner, except that σ_1 is the collision diameter for a hydrogen atom colliding with a hydrogen molecule, and $\bar{\tau}$ is now the mean life of the quasi-molecule H_3. The number of three-body collisions of this type is then given by

$$\begin{aligned} Z_3 &= 2\sqrt{2\pi} N_L^2 \sigma_2^2 \left(\frac{4RT}{3M}\right)^{1/2} [C_H][C_{H_3}] \\ &= 8\pi\sqrt{2}\, N_L^3 \frac{RT}{M}\, \sigma_1^2 \sigma_2^2\, \tau\, [C_H]^2[C_{H_2}] \end{aligned} \qquad (3)$$

or, on introducing the statistical weight factor $1/4$

$$Z_3^* = 2\pi\sqrt{2}\, N_L^3 \frac{RT}{M}\, \sigma^2{}_2 \sigma_1^2\, \bar{\tau}\, [C_H]^2[C_{H_2}] \qquad (4)$$

where σ_2 is the effective diameter for the collisions of H with H_3.

We may safely assume that σ_1 is about the same as Steiner's σ_{AA}, that is, 2.5–3.5 $\times 10^{-8}$ cm. The value of $\bar{\tau}$ is, however, different. In order to estimate the value of $\bar{\tau}$ we must know the potential energy curve for three hydrogen atoms. Such a curve has been calculated by Eyring and Slater (to appear in THIS JOURNAL). The theoretical curve found by these authors agrees well with the empirical curves given by Lennard-Jones.[2] The curve consists of the coulombic energy, less one-half the interchange energy, plus the van der Waals energy for two hydrogen atoms. There is no minimum in this curve such as that in the curve for two hydrogen atoms, and any definition of the collision distance is somewhat arbitrary. A hydrogen atom with the mean thermal energy of 600 cal. will be at a distance of 2.35 $\times 10^{-8}$ cm. from the hydrogen molecule when it is brought to rest. If we assume that the molecule and atom are in contact when the potential energy between them is one-tenth of its maximum value of 600 cal. a simple calculation shows that the time of contact is 6.58 $\times 10^{-14}$ sec.

We may now use the values we have found for σ_1 and $\bar{\tau}$ to calculate σ_2 from the experimentally found rate of reaction. If we assume that all

[2] *Cf.* Fowler, "Statistical Mechanics," Cambridge, 1929, Chap. X.

of the recombination with H_2 as the third body takes place by this mechanism we find that σ_2 lies between 3.6 and 5.5 $\times$ 10^{-8} cm. Since the recombination probably takes place by both this mechanism and Steiner's the true value of the diameter σ_2 is somewhat smaller.

On the other hand, if we assume σ_2 to be equal to Steiner's σ_{AM}, which is not unreasonable, we find that our mechanism will go at a rate three to six times the rate of Steiner's mechanism.

CONTRIBUTION FROM THE
FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

RECEIVED MARCH 10, 1932
PUBLISHED JUNE 6, 1932

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE]

A STUDY OF MOLECULAR ORGANIC COMPOUNDS. IV.[1] THE MOLECULAR ORGANIC COMPOUNDS OF PHENOL, THEIR PARACHORS AND REFRACTIVITIES[2]

BY C. A. BUEHLER, J. H. WOOD, D. C. HULL AND E. C. ERWIN

RECEIVED NOVEMBER 6, 1931 PUBLISHED JUNE 6, 1932

The molecular organic compounds of phenol, as a group, represent one of the simplest types. These compounds, although possessing fairly sharp melting points, decompose so readily into the original components that attempts to gain any information as to their structure by chemical methods have been unsuccessful. In the present investigation two physical methods have been applied to the study of the structure of some of these molecular compounds.

In Table I are listed the compounds which have been isolated and studied. Most of these have only previously been shown to exist by their freezing point curves. Worthy of note are the great number of them, the usual molecular ratios of 1:1 and 2:1 and the fact that the second components all contain amino groups.

The parachors as determined, both for some of the components and their molecular compounds, by the formula of Sugden[3] are given in Tables II and III. Among the components it is to be noted that the observed parachors are lower than the calculated values and with increasing temperature a steady rise occurs much in the same way as with the alcohols and fatty acids.[4] The same relation exists among the molecular compounds although the temperature coefficients and the differences between

[1] Contribution III, THIS JOURNAL, 53, 4094 (1931).

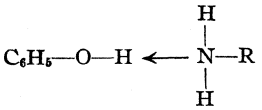
[2] Parts of this paper are taken from the Masters' Theses presented by David C. Hull and E. C. Erwin at the University of Tennessee.

[3] Sugden, "The Parachor and Valency," George Routledge and Sons, Ltd., London, 1930, p. 30.

[4] Sugden, Ref. 3, p. 167.

the observed and calculated values are greater here. It is likely that we are dealing in both cases with association, the amount of which becomes less and less with an increase in temperature.

It is not possible, at present, by any known method to find the degree of association at any one temperature. However, the differences between the observed and calculated values of the parachors for the molecular compounds, with decreasing temperature, do approach a maximum negative value. According to Sugden[5] such a negative value is due to a bond consisting either of a pair of electrons (the semi-polar double bond) or of a single electron. Although the latter is used freely by Sugden[5] it finds less favor in other quarters.[6] We are discarding it as a possibility since the stability of the compounds concerned does not seem to be of a sufficiently low order to warrant such a type of union. There remains the semipolar double bond which (excluding ring formation, which does not seem likely due to the fact that an unstable four-membered ring would result) may account for the type of formula recently advanced:[7]



From Sidgwick's[8] work among the ortho substituted phenols it appears that the semipolar bond above has the usual value of -1.6 plus a value of -12.8 due to the rise in covalency of the hydrogen from 1 to 2. The total value, -14.4, as Table III shows, may in general be considered as the maximum for the differences between the observed and calculated parachors and the formula above may, therefore, be considered as the most probable for the molecular compounds of phenol.

The refractive indices for the components and their molecular compounds are shown in Table IV and the molecular refractions as obtained by the Lorenz and Lorentz formula are given in Table V. A comparison of the observed and calculated molecular refractions at 20° shows in general, in the case of the components, some optical exaltation, while with the molecular compounds optical depression is usually exhibited. In either case the optical exaltation for any amine is greater than that for the molecular compound which it forms with phenol. Although this reduction in refraction was originally attributed[9] to an increase in the valence of the nitrogen of the amine it may be considered, by the more modern interpreta-

[5] Sugden, Ref. 3, p. 131.

[6] Sidgwick and Bayliss, *J. Chem. Soc.*, 2033 (1930); Pauling, THIS JOURNAL, **53**, 3229 (1931).

[7] Buehler, Alexander and Stratton, *ibid.*, **53**, 4094 (1931).

[8] Sidgwick and Bayliss, Ref. 6, p. 2032.

[9] Eisenlohr, *Ber.*, **44**, 3188 (1911).

tion of Smyth,[10] as being due to the attachment of the hydrogen of the phenol to the nitrogen of the amine as proposed in the formula above. In Table V these differences are shown in the last column, which is really a comparison of the differences between the observed and calculated molecular refractions of the molecular compounds with the sum of the like differences of the two components.[11] It is obvious that if the mixture law were true these values would all be zero. Since they are all negative in value they may be interpreted in terms of a union between the two molecules. The differences, which are approaching zero with increasing temperature, are small doubtless due (1) to the partial dissociation of the molecular complex and (2) as Smyth has suggested to the counterbalancing effect produced by the weakening of the forces which the hydrogen exerts on the oxygen of the phenol.

Experimental Part

The preparation, purification and analysis of the molecular compounds were accomplished in the main from the second components and by the methods already described. In doubtful cases freezing point curves were constructed.

Purification of Components.—The components concerned either as individuals or otherwise in the parachor and refractivity determinations were specially purified as stated below.

Phenol.—Method of Sidgwick and Bayliss;[12] m. p. (corr.) 40.5°.

Aniline.—The commercial product, distilled twice, was converted into acetanilide which was crystallized three times from water containing a little acetic acid. This solid was hydrolyzed, the aniline obtained being treated with acetone to remove thiophene by the method of Hantzsch and Freese.[13] The amine was finally recovered from the hydrochloride by treatment with sodium carbonate solution and, after being dried over solid potassium hydroxide and fractionally distilled twice, it boiled at 184.3° (corr.).

***o*- and *m*-Toluidines.**—In general, by the method of Berliner and May;[14] b. p.'s *o*- 199.3° (corr.), *m*- 203.0° (corr.).

***p*-Toluidine.**—In general, by the method of Gans and Harkins;[15] m. p. 43.4° (corr.).

4-Amino-1,3-dimethylbenzene.—The c. p. product, first distilled, was converted into the hydrochloride, which was fractionally crystallized twice from absolute alcohol

[10] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 160.

[11] This method of comparison seemed advisable because of the unreliability of the atomic refractions at temperatures above 20° as well as that of nitrogen at 20°. This latter value varies so much even among aromatic primary amines that the mean loses much of its significance. In contrast to the parachor discussion the differences between the observed and calculated values of the components are attributed to the difficulty with the atomic refractions and not to association.

[12] Sidgwick and Bayliss, Ref. 6, p. 2027.

[13] Hantzsch and Freese, *Ber.*, **27**, 2966 (1894).

[14] Berliner and May, THIS JOURNAL, **49**, 1008 (1927).

[15] Gans and Harkins, *ibid.*, **52**, 2292 (1930).

and then twice from water. The product thus obtained was treated with sodium carbonate solution to free the xylidine which was dried over solid potassium hydroxide and then fractionally distilled twice under reduced pressure; b. p. 214.3° (corr.).

Physical Measurements.—Surface tensions were determined by the maximum bubble pressure method of Sugden.[16] The bubbler was immersed in a constant temperature bath and readings of the manometer level were made with a cathetometer. Highly purified benzene was used in the determination of the diameter of the larger bubbler tube after the diameter of the smaller one had been measured by a filar micrometer.

Densities of the liquids were determined with an ordinary 10-cc. pycnometer; the densities of the vapors at the temperatures employed were negligible and were, therefore, undetermined.

The refractivity measurements at 45, 60 and 80° were made by a Pulfrich refractometer.

TABLE I

MOLECULAR COMPOUNDS OF PHENOL

Second component	M. p., °C. (corr.)	F. p., °C. (litr.)	Color	Mol. ratio	N, % Calcd.	N, % Found	
Aniline	32.6	32[a]	Colorless	1:1	7.48	7.64	7.53
o-Toluidine	35.6	34[b]	White	1:1	6.96	6.93	6.78
m-Toluidine	−7[c]	...	Colorless	1:1	6.96	6.78	6.78
p-Toluidine	33.0	28.5[d]	Colorless	1:1	6.96	6.97	6.88
4-Amino-1,3-dimethylbenzene	16[c]	16[b]	White	1:1	6.51	6.37	6.41
α-Naphthylamine	29.1	28.8[d]	Purple	1:1	5.90	5.70	5.96
β-Naphthylamine	84.4	83.5[b]	White	1:1	5.90	5.96	5.70
Benzidine	128.4	...	Light gray	1:1	10.07	10.25	10.27
o-Phenylenediamine	44.2	43.5[e]	Brown	1:1	13.85	13.98	14.08
o-Phenylenediamine	29.7	29.5[e]	Colorless	4:1	5.78	5.63	5.67
m-Phenylenediamine	58.0	52.6[e]	Gray	3:2	11.23	11.09	11.11
p-Phenylenediamine	98.6	...	Reddish-brown	1:1	13.85	13.87	13.91
p-Phenylenediamine	106.5	105[e]	Dark brown	2:1	9.45	9.61	9.38
Urea	61.5	60.4[d]	White	2:1	10.07	10.09	10.22
Acetamide	42.9	40.8[f]	White	2:1	5.66	5.59	5.69
Acetamide–water	42.1	...	Pink	2:1:1	5.28	5.26	5.17
Benzamide	31.0[c]	23.5[f]	White	2:1	4.53	4.48	4.62
Diethylamine	12[c]	...	Pink	1:1	8.37	8.27	8.23
Pyridine	−19[c]	−10[g]	White	1:1	54.39[h]	54.46	54.40
Pyridine	4[c]	5[g]	White	2:1	70.41[h]	70.62	70.38

[a] Melting point of the compound first obtained by Hübner, *Ann.*, **210**, 342 (1881).
[b] Kremann, *Monatsh.*, **27**, 91 (1906).
[c] Freezing point, ±1° accuracy.
[d] Philip, *J. Chem. Soc.*, **83**, 814 (1903).
[e] Kremann and Petritschek, *Monatsh.*, **38**, 405 (1917).
[f] Kremann and Wenzig, *ibid.*, **38**, 479 (1917).
[g] Bramley, *J. Chem. Soc.*, **109**, 474 (1916).
[h] Percentage of phenol; determined by titration of tribromophenol with alkali.

[16] Sugden, Ref. 3, p. 208.

Table II

DENSITIES, SURFACE TENSIONS AND PARACHORS OF COMPONENTS

Compounds	Temp., °C.	d	γ	P (obs.)	P (calcd.)	P (obs.) − P (calcd.)
Phenol	50	1.0499	37.74	222.0[17]	227.1	−5.1
	70	1.0328	35.45	222.2		−4.9
	90	1.0150	33.35	222.7		−4.4
	120	0.9885	30.18	223.0		−4.1
	150	.9588	26.77	223.1		−4.0
Aniline	50	.9957	40.10	235.2	236.7	−1.5
	70	.9780	37.63	235.7		−1.0
	90	.9602	35.22	236.1		−0.6
	120	.9338	31.60	236.3		−0.4
	150	.9052	28.07	236.6		−0.1
o-Toluidine	50	.9743	37.49	272.0	275.7	−3.7
	70	.9575	35.18	272.4		−3.3
	90	.9405	32.92	272.7		−3.0
	120	.9152	29.70	273.1		−2.6
	150	.8890	26.52	273.3		−2.4
m-Toluidine	25	.9851	37.73	269.4	275.7	−6.3
	50	.9653	35.62	271.0		−4.7
	70	.9490	33.40	271.3		−4.4
	90	.9331	31.59	272.1		−3.6
	120	.9068	28.61	273.1		−2.6
	150	.8811	25.58	273.3		−2.4
p-Toluidine	50	.9619	34.88	270.5	275.7	−5.2
	70	.9444	32.80	271.3		−4.4
	90	.9276	30.89	272.2		−3.5
	120	.9020	28.16	273.5		−2.2
4-Amino-1,3-dimethylbenzene	25	.9723	36.75	307.2	314.7	−7.5
	50	.9520	34.46	308.2		−6.5
	70	.9355	32.38	308.8		−5.9
	90	.9197	30.39	309.1		−5.6
	120	.8950	27.31	309.3		−5.4
	150	.8695	24.45	309.7		−5.0

TABLE III

DENSITIES, SURFACE TENSIONS AND PARACHORS OF MOLECULAR COMPOUNDS

Compounds	Temp., °C.	d	γ	P (obs.)	P (calcd.)[a]	P (obs.) − P (calcd.)
Phenol·aniline	50	1.0289	39.17	454.9	463.8	− 8.9
	70	1.0112	36.99	456.3		− 7.5
	90	0.9932	34.90	457.9		− 5.9
	120	.9658	31.42	458.7		− 5.1
	150	.9366	27.96	459.4		− 4.4
Phenol·*o*-toluidine	50	1.0153	38.12	492.2	502.8	−10.6
	70	0.9976	35.82	493.2		− 9.6
	90	.9794	33.53	494.2		− 8.6
	120	.9522	30.16	495.0		− 7.8
	150	.9240	26.84	495.5		− 7.3

[17] Sidgwick and Bayliss' values, Ref. 6, p. 2031, vary from 222.3 at 49.6° to 224.8 at 147.5°.

TABLE III (*Concluded*)

Compounds	Temp., °C.	d	γ	P (obs.)	P (calcd.)[a]	P (obs.) − P (calcd.)
Phenol·*m*-toluidine	25	1.0292	38.93	488.1	502.8	−14.7
	50	1.0090	36.67	490.6		−12.2
	70	0.9918	34.49	491.5		−11.3
	90	.9748	32.71	493.4		− 9.4
	120	.9485	29.74	495.2		− 7.6
	150	.9204	26.72	496.8		− 6.0
Phenol·*p*-toluidine	50	1.0084	36.18	489.1	502.8	−13.7
	70	0.9911	34.11	490.5		−12.3
	90	.9733	32.18	492.2		−10.6
	120	.9468	29.29	494.4		− 8.4
Phenol·4-amino-1,3-dimethylbenzene	25	1.0190	38.15	524.7	541.8	−17.1
	50	0.9997	35.76	526.3		−15.5
	70	.9826	33.65	527.4		−14.4
	90	.9654	31.67	528.7		−13.1
	120	.9391	28.73	530.4		−11.4
	150	.9115	25.97	532.8		− 9.0

[a] P (calcd.) = sum of P's (calcd.) of components.

TABLE IV

REFRACTIVE INDICES AT 45°

Compound	$\frac{dn}{dt} \times 10^5$ [a]	n_D^{45}	n_α^{45}	n_β^{45}
Phenol	47	1.54018	1.53498	1.55382
Aniline	53	1.57285	1.56646	1.59052
o-Toluidine	51	1.56020	1.55377	1.57610
m-Toluidine	49	1.55609	1.54992	1.57210
p-Toluidine	49	1.55397	1.54778	1.56950
4-Amino-1,3-dimethylbenzene	48	1.54729	1.54156	1.56242
Phenol·aniline	48	1.55742	1.55145	1.57270
Phenol·*o*-toluidine	48	1.55300	1.54725	1.56780
Phenol·*m*-toluidine	48	1.55036	1.54466	1.56506
Phenol·*p*-toluidine	47	1.54992	1.54422	1.56464
Phenol·4-amino-1,3-dimethylbenzene	48	1.54747	1.54192	1.56184

[a] Mean of the temperature coefficients of the D, $H\alpha$ and $H\beta$ lines.

TABLE V

VARIATION OF MOLECULAR REFRACTION WITH TEMPERATURE

Observed values at 20° calculated by use of the two temperature coefficients

Temp., °C.	MR_D (obs.)	EMR_D[a]	Temp., °C.	MR_D (obs.)	EMR_D[a]	EMR_D (M. C.) − EMR_D (C's)[b]
	Phenol			Phenol·aniline		
20	27.91	0.09	20	58.07	−0.38	−0.40
45	28.00	.17	45	58.27	− .18	− .39
60	28.06	.23	60	58.47	.02	− .31
80	28.11	.28	80	58.63	.18	− .27

TABLE V (*Concluded*)

Temp., °C.	MR_D (obs.)	EMR_D[a]	Temp., °C.	MR_D (obs.)	EMR_D[a]	EMR_D (M. C.) − EMR_D (C's)[b]
	Aniline			Phenol·*o*-toluidine		
20	30.55	− .07	20	62.83	− .24	− .37
45	30.66	.04	45	63.11	.04	− .28
60	30.72	.10	60	63.29	.22	− .21
80	30.79	.17	80	63.45	.38	− .20
	o-Toluidine			Phenol·*m*-toluidine		
20	35.28	.04	20	63.03	− .04	− .27
45	35.39	.15	45	63.26	.19	− .25
60	35.44	.20	60	63.44	.37	− .21
80	35.54	.30	80	63.59	.52	− .18
	m-Toluidine			Phenol·*p*-toluidine		
20	35.38	.14	20	63.00	− .07	− .30
45	35.51	.27	45	63.26	.19	− .26
60	35.59	.35	60	63.44	.37	− .21
80	35.66	.42	80	63.59	.52	− .23
	p-Toluidine			Phenol·4-amino-1,3-dimethylbenzene		
20	35.38	.14	20	67.76	.07	− .21
45	35.52	.28	45	68.00	.31	− .19
60	35.59	.35	60	68.19	.50	− .13
80	35.71	.47	80	68.36	.67	− .12
	4-Amino-1,3-dimethylbenzene					
20	40.05	.19				
45	40.19	.33				
60	40.26	.40				
80	40.37	.51				

[a] $EMR_D = MR_D$ (obs.) − MR_D^{20} (calcd.). The atomic refractions used are the revised values of Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911); **79**, 134 (1912). Similar calculated molecular refractions may be obtained by the refractions of the electron groups as given by Smyth, Ref. 10, p. 152. In the latter case 6.02 is used for the aromatic group,  .

[b] EMR_D (M. C.) − EMR_D (C's) is the difference between the observed and calculated molecular refractions of the molecular compounds minus the sum of the like differences for the components.

Summary

New molecular compounds of phenol have been isolated.

The densities, surface tensions and refractivities of certain of these compounds over a range of temperature have been determined.

The parachors and molecular refractions both increase with increase in temperature.

A comparison between the observed and calculated values for the parachors and molecular refractions indicates that the bond between the components in the molecular compounds has a negative value.

An electronic formula, based upon these determinations, has been proposed.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM EAST LONDON COLLEGE, UNIVERSITY OF LONDON]

THE PINACOL–PINACOLONE REARRANGEMENT. THE EXAMINATION OF SOME ORTHO-SUBSTITUTED BENZOPINACOLS

BY COLIN H. BEALE AND HAROLD H. HATT

RECEIVED NOVEMBER 13, 1931 PUBLISHED JUNE 6, 1932

It is generally recognized that the values for the relative migratory powers of aromatic hydrocarbon radicals in the pinacol–pinacolone rearrangement are least liable to error when they are obtained from studies of the rearrangement of tetraarylpinacols, for the reason that in such cases there is the least possibility of the end products of the reaction arising in any other way than by a direct pinacol–pinacolone change. In this connection *o*-substituted benzopinacols have been but little examined; of the simple compounds of this class only *sym.*-2,2′-dichlorobenzopinacol and *sym.*-2,2′-dibromobenzopinacol have been at all fully investigated.[1] These pinacols rearranged slowly and the resulting pinacolones were very resistant to attack by alcoholic potash so that a complete decomposition thereby into the corresponding triarylmethanes and aromatic acids was not effected, but it was concluded that in the rearrangements only the unsubstituted phenyl group underwent migration.

Recently Bailar[2] stated that *sym.*-2,2′-dimethylbenzopinacol and *sym.*-2,2′-dimethoxybenzopinacol could not be rearranged either by iodine and acetic acid, or by acetyl chloride and acetic acid, prolonged treatment with the latter reagent giving rise to unidentifiable oils. He considered these results to be in good agreement with the theoretical conclusions of Lagrave.[3] Bailar overlooked the fact that the rearrangement of *sym.*-2,2′-dimethylbenzopinacol had already been described[4] and that of the phenyl and *o*-tolyl groups the former had been shown to migrate the more readily.[5]

We therefore decided to repeat the rearrangement of *sym.*-2,2′-dimethylbenzopinacol (I), determining the relative migratory powers of the phenyl

[1] Koopal, *Rec. trav. chim.*, **34,** 115 (1915).

[2] Bailar, THIS JOURNAL, **52,** 3596 (1930).

[3] Lagrave, *Ann. chim.*, **10,** VIII, 363 (1927).

[4] Hatt, *J. Chem. Soc.*, 1623 (1929).

[5] Of the ten pinacols described by Bailar as new, two were already known: *sym.* 2,2′-dimethylbenzopinacol [W. D. Cohen, *Rec. trav. chim.*, **38,** 123 (1919); Boyd and Hatt, *J. Chem. Soc.*, 898 (1927)] and *sym.*-2,2′-dimethoxybenzopinacol [Cohen, *Rec. trav. chim.*, **38,** 123 (1919), and **39,** 258 (1920)].

and *o*-tolyl radicals, and also to examine *sym*.-2,2′-dimethoxybenzopinacol (II).

The Rearrangement of the Pinacols and Evidence for Their Free Radical Dissociation in Acetic Acid Solution.—The rearrangement of these pinacols with a solution of iodine in acetic acid proceeds readily, but a successful rearrangement with acetyl chloride has not been effected. The transformations with the first reagent must be practically complete, for with both pinacols 90% yields of the pinacolones were isolated. A further test was possible in the case of pinacol (II) which gives a strong green-black solution in sulfuric acid,[6] whereas the resulting pinacolones give only pale yellow-brown solutions. By means of this sensitive test it was shown that no pinacol remained after one hour's refluxing with iodine and acetic acid. Pinacol (I) rearranges at a slower rate than (II) and to be complete the treatment must be continued for eight to twelve hours according to the amount of iodine employed.

Some observations made in connection with this problem throw light upon the nature of the rearranging agent. At its boiling point a solution of iodine in acetic acid attacks the methoxyl groups of pinacol (II). For example, with a rearrangement carried out in the usual Zeisel apparatus for the estimation of methoxyl, the amount of silver iodide collected was equivalent to 1.8% of the methoxyl radicals present in the pinacol. The production of methyl iodide was attributed to the presence of hydriodic acid, which may possibly arise by a reaction such as the following[7]

$$CH_3COOH + I_2 = ICH_2COOH + HI$$

In our experiment, if the iodine had reacted completely in this way, the hydriodic acid could have attacked 1.7% of the pinacol. If sodium acetate was added to the iodine and acetic acid, the reagent was unable to effect rearrangement and the small amount of iodine present was rapidly removed. Failure to rearrange is, nevertheless, not due to lack of iodine, for no rearrangement took place when iodine was added to the solution at a rate which maintained the concentration at a value sufficient in absence of sodium acetate to effect rearrangement.

In further experiments using benzopinacol it was found that sodium acetate and iodine react alone at an appreciable rate, but in presence of the pinacol the iodine disappears more rapidly. Using sufficient iodine the pinacol is converted almost quantitatively to benzophenone. If the iodine does not suffice to convert the pinacol to the ketone, then, as the iodine is used up, the solution becomes first colorless and then rapidly acquires a distinct violet to blue color, which is the more pronounced the greater the concentration of sodium acetate. Subsequent addition of iodine reverses these color changes, and with suitable additions of iodine these variations

[6] Compare Wizinger and Fontaine, *Ber.*, **60**, 1377 (1927).

[7] Lapworth, *J. Chem. Soc.*, **85**, 41 (1904); Shaw, *ibid.*, **123**, 2233 (1923).

in color may be obtained several times. Such phenomena suggest that the benzopinacol is partially transformed into free radicals of the metal-ketyl type and of these sodiobenzophenone appears the most likely to arise, being produced in small quantities according to the equation

$$\begin{matrix}Ph_2C{-}OH\\ |\\ Ph_2C{-}OH\end{matrix} + 2CH_3COONa \rightleftharpoons \begin{matrix}Ph_2C{-}ONa\\ |\\ Ph_2C{-}ONa\end{matrix} + 2CH_3COOH \rightleftharpoons 2\begin{matrix}Ph_2C{-}ONa\\ |\end{matrix}$$

sodium acetate in acetic acid thus simulating the behavior of sodium ethoxide in ethyl alcohol[8] and of potassamide in liquid ammonia.[9] The reaction with iodine would then proceed according to the equation of Schlenk[10]

$$2\begin{matrix}Ph_2C{-}ONa\\ |\end{matrix} + I_2 = 2Ph_2C{=}O + 2NaI$$

Support for this view is found in the observation that a stream of dry air led through a solution of benzopinacol and sodium acetate in acetic acid oxidizes the pinacol to benzophenone. However, it is necessary to indicate two observations that are not quite in agreement with this view: the first, that we have failed to observe the development of a blue color in a solution of benzopinacol and sodium acetate in acetic acid before the addition of any iodine; the second, that a current of dry air is able to convert benzopinacol in boiling acetic acid into benzophenone. Alternatively, this last observation and those concerning solutions of the pinacol in acetic acid and sodium acetate could be explained by supposing partial dissociation of the pinacol into diphenylhydroxymethyl.

Experiments have shown that benzopinacol is rearranged more slowly in an acetic acid solution of iodine than by a similar equimolecular solution of hydriodic acid (containing but a slight trace of iodine). In the first solution it is possible to observe the complete disappearance of the color due to iodine and to find that the rearrangement is nevertheless complete. Since previous experiments have shown that such solutions always contain hydriodic acid, this latter would seem to be the effectual agent in such rearrangements. Whether the presence of a little iodine has a promoting influence cannot be stated; what appears more important is the hydrogen-ion concentration, any great decrease in the value of which, by the addition of sodium acetate, suppresses rearrangement.

Experimental

The Preparation of Sym.-2,2′-dimethoxybenzopinacol.—2-Methoxybenzophenone was reduced to the pinacol using zinc dust and acetic acid by the method already described for 2-chlorobenzophenone.[11] Reduction for five days at 25° gave much the better yield. The pinacol so obtained melted at 165–168° and under the microscope

[8] Schlenk and Thal, *Ber.*, **46,** 2840 (1913).

[9] Wooster, THIS JOURNAL, **50,** 1388 (1928).

[10] Schlenk, *Ber.*, **44,** 1182 (1911).

[11] Hatt, *J. Chem. Soc.*, 1629 (1929).

was seen to consist of two types of crystals: long rectangular prisms (I) and rhombic plates (II), separable by fractional crystallization from chloroform and alcohol, the former being the less soluble. Tetraarylpinacols melt with decomposition,[12] and the melting point depends upon the rate of heating. In the present two cases the melting points lie too close together to provide a method for distinguishing the pinacols. Under comparable conditions (I) melted at 173–175° and (II) at 174–176°. Either is completely liquid after heating for twenty-five minutes at 154°.

Anal. Calcd. for $C_{28}H_{26}O_4$: C, 78.83; H, 6.15. (I) Found: C, 78.72; H, 6.19. (II) Found: C, 78.75; H, 6.19.

Rearrangement of Sym.-2,2'-dimethoxybenzopinacol.—The pinacol (1.93 g.), refluxed for four hours with dry glacial acetic acid (20 cc.) and iodine (0.04 g.) and poured into 50 cc. of water containing a little sodium sulfite, gave a white crystalline precipitate, which, after filtering, washing with water, and drying at 100°, melted at 157–158° and weighed 1.7 g. (92% of theoretical). Four recrystallizations, each time employing a different solvent, raised the melting point to 161°.

Anal. Calcd. for $C_{28}H_{24}O_3$: C, 82.33; H, 5.93; mol. wt., 408. Found: C, 82.43; H, 6.15; mol. wt., 405 (in camphor).

Nevertheless, this was still a mixture of the two possible pinacolones, for rupture with alcoholic potash produced a mixture of *o*-anisic acid and benzoic acid. A second rearrangement in which the time of refluxing was one hour gave precisely the same product in 92% yield.

The Action of Alcoholic Potash on the Pinacolones.—As mentioned, Koopal was unable to transform di-ortho-substituted benzopinacolones completely into the corresponding triarylmethanes and aromatic acids. We have experienced the same difficulty when using the crude pinacolones for the estimation of the migratory powers of groups, although one of us[11] found that pure *o*-toluyl-*o*-tolyldiphenylmethane could be transformed almost quantitatively into the methane and acid. Bailar observed that occasionally with meta- or para-substituted benzopinacolones the alcoholic potash solutions became a deep brown color. He found that the values for the migratory powers obtained from such experiments were never concordant and rejected them. In all of our experiments a brown color and finally a brown precipitate were produced. For ortho substituted pinacols we believe the formation of this brown precipitate to be due to the comparatively slow rearrangement of the pinacol permitting of the simultaneous formation of the hydrol and ketone by thermal decomposition, and of the ketone by oxidation, if air is not excluded. The ketone so contaminating the pinacolone is then reduced by the alcoholic potash to the hydrol and the acetaldehyde produced resinifies.[13] Thus, if benzopinacolone, resulting from the treatment of the pinacol with iodine and acetic acid, is treated, without preliminary crystallization, with alcoholic potash, the solution does not become brown after prolonged boiling. But the brown precipitate is produced if a little benzopinacol is added to the solution, or by prolonged refluxing of the acetic acid solution of the pinacol before rearrangement. The low yields of acids we obtained (not more than 60% of the theoretical) appear to be connected with this phenomenon rather than due to incomplete fission of the pinacolones. In one case where 1.74 g. of the methoxylated pinacolone gave 0.274 g. of acids by refluxing for one hundred hours with alcoholic potash, a further like treatment of the neutral products yielded only an additional 0.016 g. Because, although the yields of acids varied considerably, their composition remained constant, we consider that the migratory powers calculated on this basis are essentially correct and have a maximum error of about 5%.

[12] Thörner and Zincke, *Ber.*, **10**, 1473 (1877).

[13] Compare Montagne, *Rec. trav. chim.*, **27**, 327 (1908); **31**, 298 (1912).

Determination of Migratory Powers.—The pinacol (2 g.) was converted to the pinacolone as already described, the latter dried, transferred to an all-glass apparatus and there refluxed for one hundred hours with a solution of potassium hydroxide (5 g.) in absolute alcohol (50 cc.). This solution was poured into 300 cc. of water and the liquors evaporated three times to two-thirds of their bulk to remove the alcohol completely. The insoluble material was extracted with chloroform or benzene, the aqueous liquors acidified and extracted with one of the above solvents and these last extracts dried, evaporated, and the acids dried to constant weight at room temperature.

The equivalent weight of the mixed acids was determined by one or more of the following methods. (I) The methoxyl content was determined by the usual Zeisel method. To obtain reliable results it was necessary to remove all foreign ethoxyl containing substances, which was accomplished by repeated evaporation of the alkaline liquors and the use of chloroform or benzene as extractant as described above. (II) By titration with standard baryta solution. (III) The salicylic and benzoic acids generated in method (I), after decolorization in aqueous solution with sulfurous acid, were extracted in benzene, the solution washed with water, evaporated and the salicylic acid estimated according to the method of Bougeault.[14] After removing the purple precipitate of "tetraiododiphenylene quinone," benzoic acid was extracted from the aqueous filtrates and identified in the usual way. The yields of benzoic acid were low but agreed fairly well with the figures obtained by the above three methods.

The estimations of the equivalent weight of the mixed acids by the three methods are in good agreement. Owing to the extra manipulation, method (III) is probably the least accurate. Some of the results are set out in Table I; from them the mean values of the relative migratory powers of the phenyl and *o*-anisyl groups are found to be 1.00 and 0.30.

TABLE I

No.	Pinacol, g.	Yield of acids, g.	Percentage by weight of *o*-anisic acid in the mixed acids: Method (I)	Method (II)	Method (III)
1	2.018	0.274	81.0	80.9	..
2	2.002	.280	81.7	..	77
3	2.000	.327	..	..	81.6
4	1.926	.390	..	..	83.3

2-Methylbenzophenone and 2,2'-Dimethylbenzopinacol.—Several processes have been given for the preparation of 2-methylbenzophenone. We have found that 2-methylbenzohydrol can be oxidized to this ketone almost without any side chain oxidation. On the other hand, Zincke,[15] Senff,[16] and others found that complete oxidation of the methylene group in the benzyltoluenes could not be accomplished without considerable oxidation of the methyl group.

2-Methylbenzohydrol was readily obtained from *o*-tolylmagnesium bromide and benzaldehyde. 10 g. of the hydrol was added with vigorous stirring to a mixture of 20 g. of potassium dichromate, 16.5 cc. of concentrated sulfuric acid and 95 cc. of water. The mixture was stirred at 45–50° for half an hour and then poured into aqueous sodium hydroxide. After almost neutralizing with sulfuric acid, extraction with ether gave 9.3 g. of almost pure ketone.

Reduction of the ketone with zinc dust and acetic acid proceeded smoothly, giving the pinacol, m. p. 160–161° (from chloroform and alcohol). Heated with glacial acetic

[14] Bougeault, *Compt. rend.*, **146,** 1403 (1908); *J. pharm. chim.*, [VI] **28,** 145 (1908).

[15] Zincke, *Ann.*, **161,** 93 (1872).

[16] Senff, *ibid.*, **220,** 237 (1883).

acid and iodine for twelve hours, the pinacol yielded the stable pinacolone.[11] Apart from this extra time required for the rearrangement, the relative migratory powers of the phenyl and *o*-tolyl groups were determined essentially according to the procedure for the previous case.

Ninety-seven to ninety-eight per cent. of the theoretical yields of the crude pinacolone were obtained. In three experiments the weights of acid obtained from 1.834, 1.816 and 2.000 g. of pinacol were, respectively, 0.267, 0.259 and 0.329 g. The equivalent weights determined by method (II) were 136.3, 135.1 and 138.2 (*o*-toluic acid requires 136), showing that there is almost exclusive migration of the phenyl group.

The Oxidation of Benzopinacol in Acetic Acid Solution.—(A) One gram of benzopinacol was added to a mixture of 10 cc. of pure acetic acid,[17] 1 g. of iodine and 2 g. of fused sodium acetate. The mixture was refluxed for one-half hour, excluding moisture, cooled and poured into dilute sulfurous acid. The crystalline benzophenone was filtered off and dried to constant weight (0.98 g.). It melted at 45–47°; 48–49° after one crystallization. In a second experiment the crude benzophenone was refluxed with alcoholic potash and the organic acids produced were estimated as in the fission of a pinacolone; 0.008 g. of benzoic acid was produced.

(B) Two grams of benzopinacol, 2 g. of sodium acetate and 20 cc. of acetic acid were refluxed on an oil-bath in a current of dry air, freed of carbon dioxide. After five hours the products were poured into water and the insoluble matter filtered off. The aqueous liquors did not liberate iodine from potassium iodide solution and experiments showed that had sodium peroxide been produced it would have been destroyed under the conditions of the experiment. The solid product, 1.85 g., was separated with petroleum ether into benzopinacol (0.5 g.) and benzophenone (0.9 g.). The crude material gave a light orange color with sulfuric acid but no benzhydrol could be isolated. In an experiment where the air was replaced by nitrogen, 80% of the pinacol was recovered in a state of purity.

(C) The reaction was carried out as in (B) but in absence of sodium acetate. The oxidation did not proceed so smoothly; using 1.9 g. of benzopinacol there were isolated 0.9 g. of benzophenone and 0.2 g. of benzopinacol.

Conclusion

Sym.-2,2′-dimethylbenzopinacol and *sym.*-2,2′-dimethoxybenzopinacol have been rearranged. From the rearrangement of the second pinacol, a value is obtained for the migratory power of the *o*-anisyl group (0.30) which exceeds that of the *m*-anisyl group (0.20). Lagrave's generalizations are therefore incorrect, in so far as they predict, as Bailar states, the inability of these pinacols to rearrange and of all *o*-substituted groups to undergo migration.

The present observations stand in agreement with the previously existing data in this field. Thus, there seems to be no case of a di-ortho-substituted benzopinacol that has failed to rearrange. And again, although the *o*-anisyl group is the first simple *o*-substituted group whose migration in the rearrangement of tetraarylpinacols has been established, some closely related groups were known to migrate. Examples of this kind occur in the rearrangement of bis-diphenylene-ethylene glycol[18] and of 1,1-diphenyl-2,2-

[17] Purified according to the method of Orton and Bradfield, *J. Chem. Soc.*, **125**, 960 (1924).

[18] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

diphenylene-ethylene glycol,[19] where in terms of the Tiffeneau–Meerwein mechanism the migration of the "ortho-linked" group is enforced. Observations have also been made pointing to the ability of similar groups to migrate where this does involve competition with the phenyl group. Elbs[20] found evidence for this in the case of the 2,5-dimethylphenyl group, and in the tetraarylpinacol series the α-naphthyl group appears to have a greater migratory power than the phenyl group, while its resemblance to an ortho-substituted phenyl group is well known.[2,20,21]

The data concerning symmetrical di-ortho-substituted benzopinacols may be regarded in the following way. For the corresponding para compounds the series:

$$p\text{-}CH_3OC_6H_4— > p\text{-}CH_3C_6H_4— > p\text{-}C_6H_5C_6H_4— > p\text{-}C_2H_5C_6H_4— > p\text{-}IC_6H_4— > C_6H_5— > p\text{-}BrC_6H_4— > p\text{-}ClC_6H_4—$$

is obtained when the migrating groups are arranged in order of their decreasing migratory power. For the ortho compounds this order is modified by the superposition of an "ortho effect." This "effect" may not be entirely sterical in nature,[22] but at present the data agree with the simple assumption that the essential difference between the migration of ortho and para substituted radicals is that the former is rendered much more difficult by opposition of a sterical kind. Although sterical effects cannot yet be evaluated with certainty, the earlier investigations,[23] the work of Kindler[22] and the calculations from x-ray analysis,[24] all agree in the order of increasing sterical effect:

$$o\text{-}H < o\text{-}CH_3 \text{ and } o\text{-}OH < o\text{-}Cl < o\text{-}Br \text{ and } o\text{-}NO_2$$

Moreover, that it is difficult to attach three *o*-tolyl groups to the same carbon atom by means of the Grignard reagent,[11] whereas, by this means, the addition of three *o*-anisyl groups takes place readily,[25] may be taken to indicate that sterical opposition to the *o*-tolyl group is much greater than to the *o*-anisyl group.

The formation of a series indicating the order of increasing migratory power for ortho-substituted radicals can only be obtained by the superposition of this "ortho effect" upon the series for para radicals when the exact relationship between these two quantities is known. But however this combination is to be effected, it can be seen that it must give the order

$$o\text{-}CH_3OC_6H_4 > o\text{-}CH_3C_6H_4— > o\text{-}ClC_6H_4— \text{ and } o\text{-}BrC_6H_4—$$

which is in agreement with the results so far obtained

$$o\text{-}HC_6H_4— > o\text{-}CH_3O\ C_6H_4— > o\text{-}CH_3C_6H_4—, o\text{-}ClC_6H_4—, o\text{-}BrC_6H_4—.$$

---

[19] Meerwein, *Ann.*, **396**, 200 (1913).

[20] Elbs, *J. prakt. Chem.*, [II] **35**, 477 (1887).

[21] Bachmann and Shankland, THIS JOURNAL, **51**, 306 (1929).

[22] Compare Kindler, *Ann.*, **464**, 278 (1928).

[23] Werner, "Lehrbuch der Stereochemie," 1904, p. 377.

[24] Adams and Stanley, THIS JOURNAL, **52**, 1200 (1930).

[25] Baeyer and Villiger, *Ber.*, **35**, 3025 (1902).

Summary

Sym.-2,2′-dimethylbenzopinacol and *sym.*-2,2′-dimethoxybenzopinacol have been rearranged to the corresponding pinacolones and the relative migratory powers of the phenyl, *o*-tolyl and *o*-anisyl groups have been determined.

Benzopinacol is oxidized by gaseous oxygen in acetic acid solution, either with or without the addition of sodium acetate, to benzophenone. The same oxidation is accomplished much more rapidly by a solution of iodine and sodium acetate in acetic acid.

EAST LONDON COLLEGE, UNIVERSITY OF LONDON
UNIVERSITY COLLEGE, SOUTHAMPTON

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF THE JOHNS HOPKINS UNIVERSITY SCHOOL OF MEDICINE]

CHEMICAL INVESTIGATION OF RAUWOLFIA CAFFRA. I. RAUWOLFINE

BY J. B. KOEPFLI

RECEIVED DECEMBER 10, 1931 PUBLISHED JUNE 6, 1932

The genus *Rauwolfia*, belonging to the natural order *Apocynaceae*, is widespread throughout the tropics and some forty-two species are known. Although most species are actively poisonous and many are reputed to possess medicinal value, information concerning their chemistry or pharmacology is extremely meager. There are occasional references in the literature wherein the investigators[1] lay claim to having obtained active crystalline bodies from some of the East Indian *Rauwolfia* but the investigations were limited in scope and the reports are vague. Accordingly, when a supply of the bark of a South African species of *Rauwolfia* became available, the present investigation was undertaken with the hope that some definite information would be forthcoming concerning the constituents of the bark responsible for the physiological activity and, furthermore, that if chemical individuals could be isolated, a study of their properties from a chemical and pharmacological viewpoint might prove of value.

The only available information concerning the South African *Rauwolfia* under investigation is contained in a report[2] from which the following facts are taken. An investigation was made of the nature of the active principle of the so-called "Quinine Tree" of the Transkei, the "*Umjela*" as it is known by the natives. This tree, now identified as *Rauwolfia caffra* (formerly as *Tabernaemontana ventricosa*, Hochst), grows in the Gxwaleni

[1] Wehmer, "Die Pflanzenstoffe," G. Fisher, Jena, 1931, Vol. ii, p. 981; Greschoff, *Ber.*, **23**, 3543 (1890).

[2] Juritz, "Report of the Senior Analyst for the Year 1901," Cape Town, 1902, p. 58.

forest in the Nyanduli district and in the Mpami forest, Elliotdale, where specimens four feet in diameter and fifty feet in height are known to occur. The bark has a bitter taste and is reputed to have the well-known therapeutic properties of quinine. No alkaloids of the cinchona group were detected in the bark but needle-shaped crystals, which were thought to represent a new alkaloid, were isolated from a chloroform extract of the bark. The report concludes with a description of the properties of the crystals which, beyond the fact that they gave a crimson lake (Vitali's test), need not be included here as there is no evidence that an individual alkaloid had been isolated.

The present communication describes the progress made thus far in the investigation of this bark. Three crystalline basic substances have been obtained, one in sufficient quantity to permit of its more detailed study. The name "rauwolfine," derived from the generic name of the tree, is suggested for this base. The other two bases are designated Base A and Base B, respectively, until more is known concerning their chemistry and possible relationship to rauwolfine.

The properties of rauwolfine, such as its apparent instability in solution and in particular its insolubility in all solvents immiscible with water, leave much to be desired in the method used for its isolation from the bark. For the sake of brevity, therefore, only an outline of the operations performed is presented in this paper; a more detailed description is reserved for future communications when the information now available will no doubt have led to more efficient methods. Lastly, certain chemical aspects of rauwolfine, aside from its possible pharmacological importance, seem of sufficient interest to warrant the further efforts which are being made with a view to elucidating the chemical constitution of the base.

Experimental

Material.—Through the kind coöperation of the Division of Plant Industry of the Department of Agriculture and the Forest Department of the Union of South Africa, a supply of the dry bark of *Rauwolfia caffra* Sonder (National Herbarium, Pretoria No. 3358) has been made available for this investigation. The material was collected in 1926, in the Mzwane Forest, Mtambalala Patrol, District Port of St. John's, Transkei, and after arrival in Baltimore was ground and stored in sealed containers.

Extraction of the Bark.—Ten kilograms of the finely ground dry bark[3] was completely extracted with hot petroleum ether (b. p. 30–60°) which yielded upon evaporation 100 g. of a light yellow waxy material that solidified in the ice chest and had a characteristic tea-like odor. This material gave negative tests for alkaloids and a portion was set aside for possible future investigation.

After petroleum ether extraction the ground bark was covered with 93% ethanol and boiled for five minutes. When cool the material was collected on a filter, transferred to a percolator and continuously extracted with fresh portions of cold 93%

[3] This opportunity is taken to thank the Directors and Laboratory Staff of Hynson, Westcott and Dunning for conducting the petroleum ether and ethanol extractions.

ethanol over a period of several weeks. When 240 liters of solvent had been used, the last percolates were still highly colored and gave copious precipitates with Mayer's reagent. The material was therefore exhausted further with 250 liters of 93% ethanol or until the percolate was but slightly colored and a test portion gave a negligible precipitate with Mayer's reagent. The last 250 liters of percolate, when concentrated under diminished pressure to 1.5 liters and placed in the ice chest for three weeks, deposited 3.5 g. of a crystalline substance which upon investigation proved to be *dl*-inosite melting at 223–224°.

The combined ethanol extracts of the bark were taken to virtual dryness under diminished pressure at 40°, which left 1040 g. of a brown varnish-like residue (representing 10% of the weight of the dry bark). The solid residue was covered with 1.5 liters of water and distilled with steam for five hours. An ethereal extract of the 3.5 liters of distillate yielded 6 g. of a sweet-smelling essential oil, together with 5 g. of *o*-hydroxybenzaldehyde, identified by means of its phenylhydrazone.

The flask containing the residue which had been subjected to steam distillation was allowed to stand overnight. The dark red supernatant liquid was then decanted from 700 g. of tarry residue and diluted with its own volume of water. After standing for several days the solution was filtered from 200 g. of an acid-insoluble resinous precipitate and concentrated to 2 liters under diminished pressure at 40°. After standing overnight in the ice chest the deep red solution, which appeared perfectly clear and was faintly acid to litmus, was repeatedly extracted with chloroform.

Base A.—The 3 liters of chloroform extract, after washing and drying and removal of the solvent, yielded 30 g. of a dark red viscous gum from which 0.015 g. of a crystalline alkaloid, designated Base A, was isolated after a series of operations involving precipitations with sodium carbonate and sodium hydroxide, together with extractions by means of dilute acid and ether. The base may be extracted from an alkaline solution with ether but is apparently insoluble in dry ether when crystalline. It is insoluble in water and petroleum ether but soluble in alcohol, chloroform and acetone and may be best crystallized from hot benzene and petroleum ether, from a mixture of which it separates in tufts of hair-like colorless needles melting at 294–295° (uncorr.) to a dark brown liquid. The Base A yields a yellow crystalline platinic chloride, a purple amorphous auric chloride and an amorphous picrate. It dissolves in concentrated sulfuric acid without color but produces a brilliant orange in concentrated nitric acid and a violet coloration fading to brown with Vitali's reagent. The base is precipitated from acid solution by sodium hydroxide, sodium carbonate and ammonium hydroxide in excess.

The main watery solution, together with the washings of the chloroform extraction, was reduced to 2 liters in volume and at the same time freed from dissolved chloroform by evaporation under diminished pressure at 40° and then precipitated with 150 g. of neutral lead acetate. After removal of the lead precipitate by filtering, the filtrate was deleaded with hydrogen sulfide, the excess acetic acid partially neutralized by addition of 20 g. of sodium carbonate, and the solution concentrated under diminished pressure at 40° to 2.5 liters. Preliminary experiments had indicated that a fractional precipitation by means of alkaline carbonate should be resorted to at this point in order to remove certain acid-soluble gums. Accordingly, 600 cc. of a 20% solution of sodium carbonate was slowly added, the supernatant liquid was decanted from the red-brown sticky precipitate which separated and the alkaline solution successively extracted with 3 liters of chloroform.

Base B.—The dark red chloroform extract, after washing with water and drying over anhydrous sodium sulfate, was concentrated to 50 cc. and allowed to evaporate at room temperature, which left 5 g. of a dark gum interspersed with crystals. Some of the crystals were picked out and examined and were obviously impure. They gave

copious precipitates with the usual alkaloidal reagents and were soluble in dilute acids; from the acid solutions the substance designated Base B could be recovered after addition of sodium carbonate in excess.

Rauwolfine

Isolation.—The alkaline solution, together with washings and some amorphous precipitate which appeared during the previous chloroform extraction, was made just acid to litmus with 100 g. of glacial acetic acid and the volume reduced to 1.5 liters under diminished pressure at 40°. To the clear liquid was slowly added a saturated solution of 150 g. of potassium carbonate. After standing for some time the solution had clarified and was decanted from the precipitated yellow gum and a further addition of 150 g. of potassium carbonate was made. This last increase in alkalinity threw down a greenish yellow amorphous, though granular, precipitate which was collected on the filter and washed with dilute potassium carbonate. It consisted for the most part of the base designated as rauwolfine. After two crystallizations from boiling water 10 g. of the base, representing 0.1% of the weight of the dry bark of *R. caffra*, was obtained as light buff-colored crystals. The base was further purified by three successive crystallizations from water, conversion into the crystalline chloride (see below) and regeneration of the free base, followed by two more crystallizations from water.

Free Base.—Rauwolfine crystallizes from water in small transparent, very light buff-colored tabular crystals (approximately 0.3 mm. in length). They appear to belong to the rhombic bipyramidal class of the orthorhombic system. The forms present, listed in the order of prominence, are the basal pinacoid, the side pinacoid, and the vertical rhombic prism. The general shape of the tablet is an elongated hexagon; two opposite angles are equal to 88°, the other four to 46° (these are the external angles). Optically the crystals show fairly high birefringence, the index of refraction is always greater than that of Canada balsam, the elongation is negative.[4] The base (dried at room temperature) has no definite melting point but when heated at a normal rate in an evacuated capillary tube it darkens at 200° and decomposes at 235–238°.

Rauwolfine in aqueous solution is strongly alkaline to litmus. It dissolves readily in all acids and solutions of its salts are neutral in reaction to litmus. The salts are not decomposed by sodium hydrogen carbonate. The free base is insoluble in sodium carbonate although soluble in sodium hydroxide, from a solution of which it is precipitated by carbon dioxide. Rauwolfine gives amorphous precipitates with all the usual alkaloidal reagents. The mercuric chloride precipitate is soluble in dilute sulfuric acid. The brown auric chloride partially reduces in the cold. The yellow picrate is decomposed on warming, likewise the orange iodo potassium iodide precipitate. The phosphotungstate is insoluble in water or alcohol. The tannate, soluble in dilute hydrochloric acid but reprecipitated by excess acid, is insoluble in ammonium hydroxide. A solution of the base in water decolorizes a neutral solution of potassium permanganate in the cold with the formation of a brown precipitate.

Rauwolfine gives two useful color reactions. A small quantity of the base dissolved in concentrated sulfuric acid produces a brilliant yellow solution. In time the color is gradually discharged; upon the addition of a drop of concentrated nitric acid to the colorless solution, a brilliant indigo-blue appears, passing rapidly through purple to a golden brown. The base dissolves in concentrated nitric acid to a deep wine-red fading to golden brown. The base does not give any marked color reaction with ferric chloride although a slight precipitate is produced in concentrated solution. Vitali's test is negative.

[4] From a cursory crystallographic examination made by Dr. J. D. H. Donnay of the Johns Hopkins University.

The behavior of rauwolfine with solvents is especially noteworthy. The crystalline base is only slightly soluble in cold water but readily so in hot (approximately one part in ten), and it is characterized by its insolubility in all the non-hydrolytic solvents tried, including pyridine and dioxane. The behavior of the base with alcohols seems exceptional—it is extremely soluble in absolute methanol but insoluble in absolute ethanol even on prolonged boiling. When 0.2 g. of the base was dissolved in 5 cc. of hot 90% ethanol and 15 cc. of absolute ethanol was added, the solution on partial cooling set to a jelly-like mass of crystals. When collected on the filter and washed with ether it formed a mat of hair-like colorless crystals weighing 0.050 g., a sample of which (dried at room temperature) decomposed at 227–229° when heated in an evacuated capillary tube. This substance turns green when heated in an air oven at 100° or when kept in an evacuated desiccator over phosphorus pentoxide. Attempts to analyze the substance gave unsatisfactory results but when it was recrystallized from water, rauwolfine of the usual crystal form and decomposition point resulted.

Although colorless specimens of rauwolfine and its salts have been obtained by precipitating them from freshly prepared solution, the application of heat necessary for recrystallization or prolonged exposure in solution always causes the appearance of some color. This color is no doubt due to products of decomposition and suggests that the base is relatively unstable in solution. An aqueous or alcoholic solution of the free base is olive-green and acidified solutions are pink; in either case the color deepens upon long standing.

Anal.[5] Calcd. (I) for $C_{20}H_{26}O_3N_2$: C, 70.17; H, 7.60. Calcd. (II) for $C_{20}H_{26}O_3N_2$ + 2.5 moles of water: N, 7.23. Found (I) (dried at 100°): C, 69.54, 69.64; H, 7.44, 7.23. Found (II) (air-dried): N, 7.13, 7.07. Subs. (air-dried) 5.007, 4.997: loss at 100°, 0.584, 0.598. Calcd. for $C_{20}H_{26}O_3N_2$ + 2.5 moles of water: 11.63. Found: 11.66, 11.97.

A Zeisel–Perkins determination of alkoxyl groups gave completely negative results with rauwolfine and since the base proved to be insoluble in camphor, the determination of its molecular weight will have to be postponed until a suitable solvent is found. Preliminary attempts to prepare an acetyl derivative or a methiodide of the base were unsuccessful.

Halogen Salts.—Rauwolfine chloride was obtained in the anhydrous form by the following procedure. To 0.1 g. of rauwolfine in 2 cc. of cold absolute methanol, 10 cc. of absolute ethanol was added together with 0.05 cc. of concentrated hydrochloric acid. The solution was filtered and, after addition of 10 cc. of anhydrous ether, placed in the ice chest overnight. Next morning 0.06 g. of the salt in the form of faintly pink, pointed plates was collected on the filter and washed with ethanol and ether.

Rauwolfine chloride plus one molecule of water may be prepared by recrystallization of the anhydrous form from water or by dissolving the free base and making the solution just acid to congo paper with hydrochloric acid. The bromide and iodide were prepared in a corresponding manner; no attempt was made to obtain their anhydrous forms.

The halogen salts of rauwolfine are slightly soluble in cold water, soluble in hot; they are furthermore soluble in methanol in the cold but soluble only with difficulty in

[5] All the analyses in this communication were performed by Dr.-Ing. A. Schoeller of Berlin-Schmargendorf by the micro method and three to five milligrams of substance was usually taken for analysis. The notation "air-dried" signifies that the substance was dried to constant weight in a current of air at room temperature. The notation "dried at 100°" signifies that the substance was dried to constant weight at 100° in a high vacuum over phosphorus pentoxide.

TABLE I

HALOGEN SALTS OF RAUWOLFINE, $C_{20}H_{25}O_2N_2 \cdot$HALIDE

Salt	M. p.,[b] (with dec.), °C.	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
Chloride anhydrous	300–303	66.57	66.80	66.70	6.93	7.07	7.00
Chloride + 1 mole H_2O	297–300 (darkens 270)	66.57	66.16	66.26	6.93	7.29	7.09
Bromide + 1 mole H_2O	250–253 (softens 245)	59.27	59.13	59.10	6.17	6.33	6.19
Iodide + 1 mole H_2O	220–225 (dec. 300+)	53.11	53.41	53.40	5.53	5.88	5.89

Salt	Nitrogen, % Calcd.	Nitrogen, % Found		Halogen, % Calcd.	Halogen, % Found		Loss at 100°, % Calcd.	Loss at 100°, % Found	
Chloride anhydrous	7.76	7.66	7.59	9.84	10.08	9.90	0	0.40	0.20
Chloride + 1 mole H_2O	7.39[a]	7.47	7.36	9.84	10.08	10.33	4.75	4.10	4.32
Bromide + 1 mole H_2O	6.62[a]	6.50	6.42	19.73	19.39	19.63	4.25	4.02	3.99
Iodide + 1 mole H_2O	5.95[a]	5.88	5.85	28.08	28.24	28.46	3.83	4.52	3.86

[a] Calculated on "air-dried" basis, + 1 mole H_2O. The other determinations were made on specimens dried at 100°.

[b] Normal rate of heating in an evacuated capillary tube.

boiling 95% ethanol. Their melting and decomposition points are not well defined and vary with the rate of heating.

Some difficulty has been experienced in measuring the optical activity of rauwolfine. However, Dr. R. T. Dillon of the Rockefeller Institute for Medical Research, who kindly made some measurements, obtained the approximate value $[\alpha]_D^{20}$ + 29° (in water) and $[\alpha]_D^{20}$ + 45° (in 95% ethanol) for the specific rotation of rauwolfine chloride.

Empirical Formula.—The empirical formulas derived from the analyses of rauwolfine and its salts are of necessity put forward only provisionally at this time. The formula $C_{20}H_{25}O_2N_2Cl$ for the anhydrous form of rauwolfine chloride seems to agree satisfactorily with the analytical data. Until a molecular weight determination can be made, the supposition seems justified that such a naturally occurring alkaloid has two nitrogen atoms rather than four or more and consequently that the molecular formula of the salt is $C_{20}H_{25}O_2N_2Cl$. In the case of the free base of rauwolfine crystallized from water, the empirical formula $C_{20}H_{26}O_3N_2 \cdot 2.5H_2O$ seems best in line with the analytical data. This would mean that the salts of rauwolfine are formed by loss of water although the possibility remains that the crystalline free base still retains some solvent of crystallization even when dried at 100° in a high vacuum over phosphorus pentoxide. No further conjecture need be made beyond the suggestion that rauwolfine may be an alkaloid of the quaternary ammonium base "type" and with the evidence at hand indicating such a possibility the nomenclature rauwolfine chloride rather than rauwolfine hydrochloride has been followed.

Pharmacological Action.—Rauwolfine or its salts, when injected into experimental animals, causes very definite pharmacological and toxico-

logical reactions.[6] The lethal dose for rats, cats, and rabbits is of the order of 35 mg. per kilogram of body weight. An intravenous or intraperitoneal injection of the drug causes, in the unanesthetized animal, restlessness and definite stimulation of the respiration, both as regards rate and amplitude, and later convulsions and cessation of the respiration occur and in some instances the heart continues to beat for several minutes.

Rauwolfine in doses of 3 mg. or more causes a definite curare-like action when injected into the lymph sacs of frogs, as evidenced by the paralysis of the motor nerve-endings in the skeletal muscles.

Rauwolfine when injected into anesthetized cats, dogs, and rabbits causes a fall in blood pressure and stimulation of the respiration—effects which can be repeatedly elicited and which also occur after a previous injection of atropine sulfate. From a pharmacological analysis it appears that the main site of action in mammals is on the brain centers, rather than in the peripheral structures. The drug has little or no effect on isolated smooth muscle.

Professor Reginald D. Manwell of the Department of Zoölogy, Syracuse University, has kindly carried out a series of tests with rauwolfine on canaries infected with *plasmodium elongatum* and *plasmodium praecox*, two species of avian malarial parasites. He found that the drug does not have antimalarial properties.

In conclusion the author desires to thank Professor John J. Abel and Dr. E. M. K. Geiling for their continued interest and encouragement, and Dr. James F. Couch for valuable criticism.

Summary

A chemical investigation has been undertaken of *Rauwolfia caffra*, a South African tree, the bark of which is reputed to possess therapeutic value. The investigation has thus far yielded three crystalline bases, one of which, identified as a new alkaloid, has been named rauwolfine and provisionally assigned the formula $C_{20}H_{26}O_3N_2 \cdot 2.5H_2O$. Some of the properties of the alkaloid, including its pharmacological action, and the preparation and properties of its halogen salts are described.

BALTIMORE, MARYLAND

[6] This information is based upon a study of the pharmacological action of rauwolfine by Dr. E. M. K. Geiling, a detailed report of which will be published in the *Journal of Pharmacology and Experimental Therapeutics*.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE BENZOHYDRYL RULE AND THE CONSTITUTION OF ALKALI TRIPHENYLETHIDES WHICH ARE STABLE IN LIQUID AMMONIA[1]

BY CHARLES BUSHNELL WOOSTER AND JOHN F. RYAN

RECEIVED DECEMBER 11, 1931 PUBLISHED JUNE 6, 1932

It has been emphasized by Kraus[2] that although the systematic investigation of the chemistry of non-aqueous solutions cannot but lead to many valuable results, substantial progress will be achieved only when such a study is made a primary objective rather than a side line, incident to other investigations. An important division of this subject deals with organic reactions, particularly reduction reactions, in liquid ammonia solution. There is a good reason for beginning an investigation of this field with the hydrocarbons. These substances exhibit a greater reactivity toward alkali metal solutions than was originally recognized[3] and some notion of the probable behavior of hydrocarbon radicals may be expected to facilitate a study of the reduction of the various types of organic compounds in which such radicals occur.

In general the reduction of hydrocarbons with alkali metals leads primarily to the formation of organo-alkali compounds which may be either stable or subject to ammonolysis in the presence of liquid ammonia. Some basis for predicting the result in particular instances has been obtained by a study of the reaction between hydrocarbons and alkali metal amides in liquid ammonia solution. This reaction is the reverse of ammonolysis

$$RH + MNH_2 \rightleftharpoons RM + NH_3 \qquad (1)$$

and its occurrence demonstrates the existence of a stable alkali metal derivative of the hydrocarbon in question.

The Benzohydryl Rule.—The action of potassium amide on some phenylated methanes and ethanes has been reported previously.[4] This study has now been extended using sodium amide and including some additional hydrocarbons.

The results obtained with the two alkali metal amides were the same. Reaction was observed with $(C_6H_5)_2CH_2$, $(C_6H_5)_3CH$, $(C_6H_5)_2CHCH_3$, $(C_6H_5)_2CHCH_2C_6H_5$, $(C_6H_5)_2CHCH(C_6H_5)_2$, $(C_6H_5)_2CHCH_2CH(C_6H_5)_2$ and tetrahydronaphthalene, but no reaction took place with $C_6H_5CH_3$, $(C_6H_5)_4C$, $C_6H_5CH_2CH_3$, $C_6H_5CH_2CH_2C_6H_5$, $(C_6H_5)_3CCH_3$, $(C_6H_5)_3CCH_2C_6H_5$ or $C_6H_5CH(CH_3)_2$.

[1] Paper presented at the Indianapolis meeting of the American Chemical Society, April, 1931.

[2] Kraus, *Chem. Rev.*, **8**, 263 (1931).

[3] Kraus and White, THIS JOURNAL, **45**, 769 (1923).

[4] Wooster and Mitchell, *ibid.*, **52**, 688 (1930).

It may be seen that in the case of the *phenylated paraffins* reaction occurred when and only when the benzohydryl group, $(C_6H_5)_2CH—$, was present in the hydrocarbon molecule. This generalization, which has been established for all the phenylated methanes, most of the phenylated ethanes and two of the phenylated propanes (including one with a tertiary structure not involving two phenyl groups), is probably applicable to the other phenylated paraffins and may be conveniently termed the *benzohydryl rule.*

This rule is closely related to that of Vorländer,[5] who pointed out that the reactivity of a hydrogen atom was increased by the presence of unsaturation in the β-position. The benzohydryl rule is more specific, however, in that it determines the amount of a particular type of unsaturation necessary to render the hydrogen atom reactive toward sodium or potassium amides in liquid ammonia at −33.5°. A comparison of the two rules furnishes two interesting suggestions. First, it indicates that the benzohydryl rule will not generally apply without modification to hydrocarbons containing other types of unsaturation than phenyl groups. This is true even when the additional unsaturation is that of a six-membered ring, as is shown by the behavior of tetrahydronaphthalene. Second, it suggests that the hydrogen atom which is replaced by alkali metal is the one attached to the aliphatic carbon atom of the benzohydryl group. This suggestion as well as other predictions based on the foregoing generalizations has been confirmed in the case of stable alkali triphenylethides prepared by various reactions including addition, substitution and molecular rearrangement. The remainder of this paper is devoted to these results which illustrate the value of the benzohydryl rule.

The Constitution of the Stable Sodium Triphenylethide.—The initial step in the reaction between sodium and triphenylethylene in liquid ammonia is the addition of sodium to the double bond

$$(C_6H_5)_2C{=}CHC_6H_5 + 2Na \longrightarrow (C_6H_5)_2CNa—CHNaC_6H_5 \qquad (2)$$

as is shown by the fact that hydrolysis of the reaction product yields 1,1,2-triphenylethane.[4] The initial product is, therefore, a 1,2-disodium-1,1,2-triphenylethane and falls within the province of the benzohydryl rule. Only one of the sodium atoms is attached to the aliphatic carbon atom of a benzohydryl group and consequently the other sodium atom is susceptible to ammonolysis.[6]

$$(C_6H_5)_2CNa—CHNaC_6H_5 + NH_3 \longrightarrow (C_6H_5)_2CNa—CH_2C_6H_5 + NaNH_2 \qquad (3)$$

[5] Vorländer, *Ber.*, **34**, 1632 (1901).

[6] The benzohydryl rule requires that *under equilibrium conditions* the system represented in Equation 3 would consist principally of the substances on the right-hand side of the arrow. Consequently, the statement made above involves the assumption that equilibrium is attained under the conditions of the experiment. In all the cases thus far investigated the ammonolysis of an unstable *organo-alkali* compound has been found to proceed rapidly.

The structure of the stable sodium compound was established by the preparation of its ethyl derivative. Ammonia was condensed on a 3-g. sample of triphenylethylene in a reaction tube,[7] and sodium was added in tenth-gram portions until a permanent blue color was obtained. After stirring for two hours, ethyl bromide diluted with dry ether was added until the color of the liquid ammonia solution was discharged. The reaction residue was washed with water and crystallized from alcohol. Rod-like crystals melting at 79–79.5° were obtained.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.31; H, 7.69. Found: C, 91.94, 92.30; H, 7.17, 7.02.

If the sodium compound actually possessed the structure tentatively assigned, the product of its reaction with ethyl bromide should be 1,2,2-triphenylbutane.

$$(C_6H_5)_2CNa—CH_2C_6H_5 + C_2H_5Br \longrightarrow NaBr + (C_6H_5)_2C(C_2H_5)CH_2C_6H_5 \quad (4)$$

This hydrocarbon is unknown, but its independent synthesis from 1,1-diphenylpropylene-(1)[8] was accomplished by the method expressed in Equations 5, 6 and 7.

$$(C_6H_5)_2C{=}CHCH_3 + 2K \longrightarrow (C_6H_5)_2CK—CHKCH_3 \quad (5)$$

$$(C_6H_5)_2CK—CHKCH_3 + NH_3 \longrightarrow (C_6H_5)_2CK—CH_2CH_3 + KNH_2 \quad (6)$$

$$(C_6H_5)_2CK—CH_2CH_3 + C_6H_5CH_2Cl \longrightarrow KCl + (C_6H_5)_2C(C_2H_5)CH_2C_6H_5 \quad (7)$$

The occurrence of the reaction expressed in Equation 5 was demonstrated by an experiment in which the propylene was slowly added to a concentrated solution of potassium in liquid ammonia so that the alkali metal was always present in large excess. The resulting organo-alkali compound was decomposed with ammonium chloride and the ammonia allowed to evaporate. The residue was a colorless oil, which was washed, dried and distilled under reduced pressure. Its properties were then compared with those of a sample of 1,1-diphenylpropane prepared by the method of Klages and Heilmann.[9] These two substances were found to be identical; both boiled at 152° under 18 mm., the density of both was 0.9783 ± 0.0001 at 25° and the refractive index (white light) was 1.5743 ± 0.0001 at 17°. It is evident, therefore, that the double bond in 1,1-diphenylpropylene is attacked by a *concentrated* solution of *excess* potassium in liquid ammonia.

The procedure described is essential, however, because in one experiment in which ammonia was condensed on a sample of the propylene and then potassium was slowly added until it was present in slight excess, the reaction with benzyl chloride produced a hydrocarbon melting at 122–124° which decolorized a solution of bromine in carbon tetrachloride and was suspected to be 1,1,4-triphenylbutylene-(1).

[7] The apparatus employed in these investigations has been described previously [Wooster, THIS JOURNAL, **51**, 1858 (1929)].

[8] Prepared by the method of Hell and Bauer, *Ber.*, **37**, 232 (1904).

[9] Klages and Heilmann, *ibid.*, **37**, 1450 (1904).

Anal. Calcd. for $C_{22}H_{20}$: C, 92.96; H. 7.04. Found: C, 93.63; H, 7.96.

This might have been formed by reactions of the type expressed in Equations 8 and 9.

$$(C_6H_5)_2C{=}CHCH_3 + K \longrightarrow (C_6H_5)_2C{=}CHCH_2K + (H) \quad (8)$$

$$(C_6H_5)_2C{=}CHCH_2K + C_6H_5CH_2Cl \longrightarrow KCl + (C_6H_5)_2C{=}CHCH_2CH_2C_6H_5 \quad (9)$$

Similar substitution reactions have been observed by Schlenk and Bergmann, and Ziegler and Schäfer.[10]

Accordingly, another sample of diphenylpropylene was added to a *concentrated* solution of *excess* potassium in liquid ammonia and after stirring the mixture for one hour just enough benzyl chloride was added to discharge the red color which appeared after the excess free potassium had reacted. The product was difficult to purify, probably because it was contaminated with low melting products of the reaction between benzyl chloride and the excess of free potassium. After three crystallizations, the substance possessed a melting point of 77–79° and was then compared with the product of the action of ethyl bromide on sodium triphenylethide.

The identity of the two hydrocarbons was shown by mixed melting points. This evidence established their constitution as that of 1,2,2-triphenylbutane, but since this conclusion is to be applied to the molecular rearrangement of an organo-alkali compound one point deserves emphasis. *The possibility of molecular rearrangements involving the carbon skeleton during the preparation of these organo-alkali compounds is excluded* by the fact that upon decomposition with ammonium chloride the sodium derivative of triphenylethylene (Reactions 2 and 3) yielded 1,1,2-triphenylethane and the potassium diphenylpropide prepared from diphenylpropylene and a *concentrated* solution of potassium in liquid ammonia yielded 1,1-diphenylpropane.

The only ethyl substitution product of 1,1,2-triphenylethane which is identical with a benzyl substitution product of 1,1-diphenylpropane is 1,2,2-triphenylbutane.[11] Therefore, the single hydrocarbon prepared by these two methods must be 1,2,2-triphenylbutane and *the tentative structure proposed for the stable sodium triphenylethide on the basis of the benzohydryl rule has been independently confirmed.*

The Constitution of the Stable Potassium Triphenylethide.—From considerations regarding the benzohydryl rule it may be predicted that the reaction between 1,1,2-triphenylethane and potassium amide follows the course indicated in Equation 10

[10] (a) Schlenk and Bergmann, *Ann.*, **479**, 78 (1930); (b) Ziegler and Schäfer, *ibid.*, **479**, 154 (1930).

[11] It can be readily seen that identical products could not be obtained in any case if more than one ethyl or benzyl group were introduced. Also, it will be shown presently that the sodium triphenylethide yields a *mono*benzyl derivative with benzyl chloride.

$$(C_6H_5)_2CHCH_2C_6H_5 + KNH_2 \longrightarrow (C_6H_5)_2CKCH_2C_6H_5 + NH_3 \quad (10)$$

yielding a substance analogous in constitution to that resulting from the action of sodium on triphenylethylene. This prediction was verified by the preparation of benzyl derivatives of the two organo-alkali compounds as follows. 1,1,2-Triphenylethane was treated with potassium amide in liquid ammonia,[7] and benzyl chloride was added to the red solution. Rapid decolorization occurred and the residue after evaporation of the ammonia was extracted with ether, the ether evaporated and the product recrystallized from alcohol. Transparent needles melting at 125–127° were obtained.

Sodium was added to a mixture of triphenylethylene and liquid ammonia until the metal was present in slight excess as shown by the blue color of the solution. Enough benzyl chloride in absolute ethereal solution was added to just discharge the color of the reaction mixture. A substance crystallizing from alcohol in needles melting at 124–126° was isolated from the ethereal extract of the reaction residue. When mixed with the product of the previous experiment, a melting point of 125–127° was found showing that the two substances are identical. The analysis also shows that only *one* benzyl radical was introduced, proving that the stable organo-alkali compounds were both *mono*-alkali triphenylethides.

Anal. Calcd. for $C_{27}H_{24}$: C, 93.10; H, 6.90; mol. wt., 348. Found: C, 92.57; 92.12; H, 6.87, 7.00; mol. wt., cryoscopic in benzene, 337.

This hydrocarbon is doubtless diphenyldibenzylmethane

$$(C_6H_5)_2CM—CH_2C_6H_5 + C_6H_5CH_2Cl \longrightarrow MCl + (C_6H_5)_2C(CH_2C_6H_5)_2 \quad (11)$$

but attempts to prepare it, independently, from benzophenone chloride and benzylmagnesium chloride

$$(C_6H_5)_2CCl_2 + 2C_6H_5CH_2MgCl \longrightarrow 2MgCl_2 + (C_6H_5)_2C(CH_2C_6H_5)_2 \quad (12)$$

were unsuccessful, the results indicating that the reaction did not proceed smoothly beyond the first step

$$(C_6H_5)_2CCl_2 + C_6H_5CH_2MgCl \longrightarrow MgCl_2 + (C_6H_5)_2CCl—CH_2C_6H_5 \quad (13)$$

The Sodium Triphenylethide Rearrangement.—Sodium reacts with 2-chloro-1,1,1-triphenylethane to give a red-colored organo-alkali compound which is stable in liquid ammonia solution[12]

$$(C_6H_5)_3C—CH_2Cl + 2Na \longrightarrow NaCl + C_{20}H_{17}Na \quad (14)$$

When this was treated with ammonium chloride the product recovered proved to be 1,1,2-triphenylethane, showing that a molecular rearrangement had occurred.

$$C_{20}H_{17}Na + NH_4Cl \longrightarrow NH_3 + NaCl + (C_6H_5)_2CH—CH_2C_6H_5 \quad (15)$$

Attempts to prepare derivatives of the sodium compound by the use of phenyl halides or carbon dioxide proved unsuccessful, but in view of its

[12] Wooster and Mitchell, THIS JOURNAL, **52**, 1042 (1930).

stability in liquid ammonia a tentative formula, $(C_6H_5)_2CNa—CH_2C_6H_5$, was assigned[12] on the basis of the benzohydryl rule. It is evident that this formula is identical with that of the sodium triphenylethide previously mentioned (Equations 2 and 3) and accordingly experiments were undertaken to prove the identity of the two compounds.

The product of Reaction 14 was first treated with benzyl chloride. However, five recrystallizations of the product failed to yield a satisfactorily purified substance. The material obtained melted at 115–117°; it was shown to be a hydrocarbon and its melting point was not decreased by admixture with the diphenyldibenzylmethane prepared previously. The product is probably diphenyldibenzylmethane but the evidence is obviously inconclusive.

Consequently the experiment was repeated using ethyl bromide. The apparatus and procedure was essentially similar to that formerly described.[12] The product was obtained after a single crystallization from alcohol in the form of transparent rod-like crystals melting sharply at 79–79.5° and was shown to be identical with 1,2,2-triphenylbutane by a mixed melting point, *thus confirming the tentative structure for this sodium compound* and showing that the reaction between 2-chloro-1,1,1-triphenylethane and sodium may be represented by Equations 16 and 17.

$$(C_6H_5)_3C—CH_2Cl + 2Na \longrightarrow NaCl + [(C_6H_5)_3C—CH_2Na] \quad (16)$$

$$[(C_6H_5)_3C—CH_2Na] \longrightarrow (C_6H_5)_2CNa—CH_2C_6H_5 \quad (17)$$

Summary

1. It has been noted that reaction between sodium or potassium amides and phenylated paraffins in liquid ammonia at its boiling point occurs only when the benzohydryl group is present in the hydrocarbon. This generalization may be conveniently termed the *benzohydryl rule.*

2. It appears probable that the alkali metal derivatives of phenylated paraffins which are stable in liquid ammonia may be prepared by the action of the alkali metal amides on the corresponding hydrocarbons and that in these reactions the alkali metal replaces hydrogen which is attached to the aliphatic carbon atom of a benzohydryl group.

3. Predictions based on the foregoing generalizations have been confirmed in the case of stable alkali triphenylethides prepared by various reactions including addition, substitution and molecular rearrangement.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE ACTION OF HALOGENS AND OF ALKYL HALIDES UPON THE SALTS OF TRIBROMOTHIOPHENOL[1]

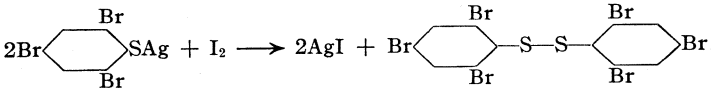
BY W. H. HUNTER AND ARTHUR H. KOHLHASE

RECEIVED JANUARY 8, 1932 PUBLISHED JUNE 6, 1932

The experiments described in this paper were undertaken in an attempt to substantiate the mechanism written by Hunter and others[2] for the decomposition of the silver salts of 2,4,6-trihalogenophenols in the presence of a trace of halogen, or simply on heating

$$2C_6H_2X_3OAg + I_2 \longrightarrow 2AgI + 2(C_6H_2X_3O-) \quad (1)$$
$$2(C_6H_2X_3O-) \longrightarrow 2(-C_6H_2X_2O-) + X_2 \quad (2)$$
$$n(-C_6H_2X_2O-) \longrightarrow (C_6H_2X_2O)_n \quad (3)$$
$$2AgI + X_2 \longrightarrow 2AgX + I_2 \quad (4)$$

In the hope that it might be possible to isolate either the thio analogs of some of the intermediates postulated in the above reactions or derivatives of these analogs, 2,4,6-tribromothiophenol was prepared and a study was made of its behavior under similar conditions. The first experiment, however, showed a marked difference in the behavior of the thiophenol as compared with the oxygen analog. On treatment of the dry silver salt, $C_6H_2Br_3SAg$, with one equivalent of iodine in dry benzene, no blue or any other color other than that of the iodine, appeared in the solution. There was an almost quantitative yield of 2,4,6,2′,4′,6′-hexabromodiphenyl disulfide, the reaction proceeding smoothly according to the equation



(5)

An amount of reddish, oily by-product, equal to 2 or 3% of the weight of disulfide, was formed. However, analysis showed it was not the analog of the polydibromophenylene oxides obtained from the corresponding phenols, being about 20% low in bromine and 60% low in sulfur.

Repetition of the experiment with one-tenth equivalent of iodine again gave an amount of disulfide equivalent to the iodine used and no other organic product. Boiling the silver salt in dry benzene produced no decomposition, while the addition of one equivalent of iodine to the boiling mixture again gave silver iodide and the hexabromodiphenyl disulfide.

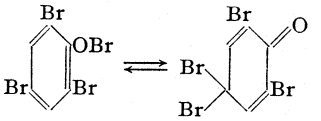
[1] The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Arthur H. Kohlhase, in partial fulfilment of the requirements for the degree of Doctor of Philosphy in 1924. This paper was prepared by the junior author after the death of Dr. W. H. Hunter, which occurred on August 19, 1931.—L. I. SMITH.

[2] For leading references, see Hunter and Seyfried, THIS JOURNAL, **43**, 135 (1921).

It was therefore expected that alkyl iodides would also fail to react in any other than a strictly normal fashion and such proved to be the case. Either cold or hot ethyl iodide or methyl iodide gave a smooth reaction leading to the ethyl or methyl thio ether in very nearly quantitative yield.

In the case of the trihalogenophenol silver salts, whatever the mechanism of the decomposition, the net result is the removal of a molecule of silver halide from the silver phenolate. This removal may, in fact, be brought about by heat alone. However, no such decomposition of the silver tribromothiophenolate could be produced by heating to various temperatures up to 180°. This greater stability of the silver thiophenolate toward heat might have been expected from a consideration of the relative stability of silver sulfide and oxide: the former melts at 842°; the oxide *decomposes* at 300–340°. Similar relations hold between some other pairs of compounds containing silver–sulfur and silver–oxygen unions.

Lauer[3] has shown that the addition of bromine in sufficient concentration to tribromophenol or its salts results in the formation of tribromophenol bromide, in which he has demonstrated the following equilibrium to obtain



(6)

Also Zincke[4] has prepared aryl sulfur halides (thiophenol halides) analogous to the compound at the left in reaction (6). It therefore seemed probable that in both the abnormal decomposition of the trihalogenated phenolates and the normal reactions of the tribromothiophenolates with halogens the first step is

$$C_6H_2X_3OAg + I_2 \longrightarrow (C_6H_2X_3OI) + AgI \quad (7)$$

$$C_6H_2Br_3SAg + Br_2 \longrightarrow (C_6H_2Br_3SBr) + AgBr \quad (8)$$

followed by

$$2(C_6H_2Br_3SBr) \longrightarrow C_6H_2Br_3S{-}SC_6H_2Br_3 + Br_2 \quad (9)$$

In the absence of a large excess of halogen the products in (7) and (8) lose halogen, reaction (7) being followed by (2) and (3), and (8) being followed by (9), giving a disulfide which is stable.

Attempts to isolate the product in (8) resulted in failure, although good evidence for its formation was obtained: treatment of the sodium salt of the tribromothiophenol with a strong aqueous bromine–potassium bromide solution resulted in a fair yield of the sulfonyl bromide. The reaction is probably (8) followed by

$$C_6H_2Br_3SBr + 2HOBr \longrightarrow C_6H_2Br_3SO_2Br + 2HBr \quad (10)$$

[3] Lauer, THIS JOURNAL, **48**, 442 (1926).

[4] Zincke, *Ann.*, **391**, 55, 57 (1912).

The product obtained in (10) and the analogs of the product in (8) which Zincke[4] has prepared, together with the equilibrium demonstrated to exist in (6), all support the existence of the products postulated in (7) and (8).

In equations (1) and (2) free radicals containing univalent oxygen are assumed as intermediates. Support for this assumption is found in the development of a marked color during the catalytic decompositions.[2]

In the course of the present work it was found that this color was instantly discharged by triphenylmethyl. Further evidence is found in the work of Goldschmidt and co-workers[5] on free radicals containing oxygen. These substances very readily rearrange or decompose. The intermediates in (1) and (2) would be peroxides or, if dissociated, free radicals. Organic peroxides are rather rare and unstable.[6] Some such decomposition as that shown in reactions (2) and (3) is therefore to be expected. In the case of sulfur compounds, on the contrary, the formation of disulfides appears to take place at every opportunity.

It is therefore to be expected that in the case of the thiphenols the reaction will stop with equations (8) and (9), the disulfide being perfectly stable.

Experimental Part

Preparation of 2,4,6-Tribromophenyl Ethylxanthate, $C_6H_2Br_3SCSOC_2H_5$.—The method is based on Leuckardt's general method for the preparation of thiophenols.[7] The chief difficulty in this preparation is the slow diazotization, due to the insolubility of the tribromoaniline in acids.

Pure 2,4,6-tribromoaniline (38 g.) was dissolved in about 75 cc. of cold 95% sulfuric acid. The clear, gray-green solution was poured slowly with stirring into 800 cc. of ice water, precipitating the tribromoaniline in very finely divided condition. The mixture was neutralized, filtered and washed once with water.

The cake was digested in a 3-liter beaker with 200 cc. of concd. hydrochloric acid; 1400 cc. of cold water and 800 g. of ice were added. While maintaining the tribromoaniline in suspension with an efficient mechanical stirrer, about 15 cc. of a solution of 9.5 g. of sodium nitrite in 100 cc. of water was added and the remainder run in drop by drop over a period of about four hours, ice being added as needed to keep the temperature near 0°. After another hour the solution was fairly clear, 97–98% of the aniline having dissolved. About 10 cc. of a 20% solution of urea was then added to destroy excess nitrous acid.

A thin paste of sodium carbonate was added with stirring, as rapidly as the frothing would permit, until most of the free acid was neutralized, after which the neutralization was continued with a *solution* of sodium bicarbonate until the neutral point was almost, but not quite, reached. The reaction mixture should be faintly acid at the end.

The solution was then filtered through an ice-cold Buchner funnel into a flask containing ice. The filtrate, amounting now to about 2600 cc., was transferred to a broad

[5] Goldschmidt and Vogel, *Ber.*, **64B**, 1744–1755 (1931).

[6] Clover, THIS JOURNAL, **44**, 1107 (1922); *cf.* benzoyl hydrogen peroxide, *Ber.*, **33**, 858, 1575 (1900); Goldschmidt, *ibid.*, **55**, 3194 (1922).

[7] Leuckardt, *J. prakt. Chem.*, [2] **41**, 179–224 (1890).

vessel; about 100 g. of ice and 100 cc. of ether were added and then a solution of 19 g. of potassium ethylxanthate in 75 cc. of water was poured in and the mixture stirred thoroughly for *not more than ten seconds*. A bright yellow oil separated, the color soon changing to orange and brown with the liberation of nitrogen.

The mixture was covered and allowed to remain *undisturbed* while slowly warming to room temperature. If disturbed while warming to room temperature, the oily material emits flashes of light and may even explode. After six hours it was warmed to 70° on a steam-bath. Most of the xanthic ester separated on the bottom as a viscous brown oil. After cooling the aqueous layer was decanted from the oil and extracted once with one-fifth volume of ether and discarded. The oil left adhering to the reaction vessel was dissolved in ether and the solution combined with the ether extract of the aqueous layer.

Solution of the oil in ether left a residue consisting of minute white crystals of di-tribromophenyl dithiolcarbonate, $(C_6H_2Br_3S)_2CO$. This red residue was saved as it also saponifies readily to the thiophenolate.

The combined ether solution of the oil was shaken thoroughly with 5% sodium hydroxide to remove any phenols, then with 5% sulfuric acid and then washed with water. The ether was evaporated and the residual oil was dried in a vacuum desiccator. The yield of oil was 40.6 g. or 81%. The yield of di-tribromophenyl dithiolcarbonate was about 10%, making a total yield of about 90% of products capable of saponification to the 2,4,6-tribromothiophenol.

The ester is a heavy, viscous, red-brown oil of characteristic, not unpleasant, odor; it is miscible with ether in all proportions, insoluble in water, forms about a 1% solution with cold alcohol and about 2% in hot alcohol. The solubility in methyl alcohol is considerably greater; benzene dissolves it readily. When boiled with alcoholic potassium hydroxide, it is saponified to the thiophenolate.

Analysis of the oil showed it was not very pure, probably containing decomposition products of the potassium xanthate.

Anal. Calcd. for $C_9H_7OBr_3S_2$: Br, 55.12; S, 14.74. Found: Br, 53.3; S, 17.5, 17.8.

Saponification of Tribromophenyl Ethylxanthate to 2,4,6-Tribromothiophenol, $(C_6H_2Br_3SH)$.—In a flask provided with a reflux condenser was placed 40.6 g. of the oily ester with 1500 cc. of methyl alcohol containing 12.6 g. of potassium hydroxide. The mixture was refluxed for about thirty minutes, until a 5-cc. sample added to water gave little or no precipitate. Too long boiling with excess alkali causes decomposition. About 80% of the methanol was then distilled off and 900 cc. of a 3% aqueous solution of sodium hydroxide was added. The mixture was warmed and stirred with a little animal charcoal and filtered. The clear, pale reddish-brown filtrate was acidified with 15% acetic acid, depositing 2,4,6-tribromothiophenol as a pale-yellow to pure white, flocculent precipitate. If not white, the precipitate was filtered off, redissolved in excess alkali, treated again with a little bone black and precipitated as before.

For the preparation of the pure thiophenol, free from disulfide, the acidification and washing of the precipitate must be carried out in an atmosphere of carbon dioxide.

The 2,4,6-tribromothiophenol crystallizes from hot alcohol as shiny, pale yellow, short needles, m. p. 115.5–115.9° corrected. It has the characteristic thiophenol odor although not nearly so pronounced or disagreeable as most of the thiophenols. It dissolves in the following solvents arranged in order of decreasing solubility: carbon disulfide, chloroform, ether, benzene, acetone, glacial acetic acid (some acetylation?), methyl alcohol, ethyl alcohol. Ethyl alcohol forms about 1% solution at 20°. It dissolves very readily in caustic alkalies. In solution or when wet it oxidizes readily, forming the disulfide.

This is the first member of the series of trihalogenated thiophenols to be prepared.

Analyses by the Carius method required heating at 285–310° for five hours; derivatives were also refractory.

Anal. Calcd. for $C_6H_2Br_3SH$: Br, 69.12; S, 9.24. Found: Br, 69.15; S, 9.97, 9.80, 9.85.

Preparation of 2,4,6-Tribromophenyl Thiolacetate, $C_6H_2Br_3SCOCH_3$.—Boiling the free thiophenol in acetic anhydride for twenty minutes and pouring the solution into dilute sodium hydroxide left the acetyl derivative as a precipitate. This was filtered off, washed and recrystallized from hot alcohol. It forms long shiny, colorless needles melting at 102.1–102.7°, corrected. It is readily soluble in hot alcohol, glacial acetic acid, and benzene.

Di-2,4,6-tribromophenyl Dithiolcarbonate, $(C_6H_2Br_3S)_2CO$.—Solution of the crude, oily tribromophenyl ethylxanthate in ether (see preparation above) left this dithiolcarbonate as a mass of minute, white crystals, very slightly soluble in ether. These are saponifiable in the same way as the xanthic ester, although requiring about 50% more time. However, the saponification of this dithiolcarbonate yielded a tribromothiophenol which was more easily purified than that from the xanthate.[8]

From hot acetone the dithiolcarbonate crystallizes in long, white, silky needles, melting at 194.2–194.7° corrected. From benzene it forms shorter, thicker needles. It is very soluble in carbon bisulfide, chloroform or benzene, slightly soluble in ether and glacial acetic acid.

Anal. Calcd. for $C_{13}H_4OBr_6S_2$: Br, 66.62; S, 8.91. Found: Br, 66.65, 66.84; S, 8.50, 8.91, 8.94. Molecular weight calcd., 655.6; found, 660.

Preparation of Silver Tribromothiophenolate, $(2,4,6)C_6H_2Br_3SAg$.—Recrystallized 2,4,6-tribromothiophenol was dissolved in an excess of halogen-free sodium hydroxide solution. The excess of alkali was nearly neutralized with 20% acetic acid, completing the neutralization with 4% acid until a slight permanent precipitate was obtained. The solution was stirred with animal charcoal and filtered. To the filtrate about 3 drops of 3% silver nitrate was then added to precipitate any halogen which might be present. The whole was shaken with bone black and again filtered. From this point the preparation was carried on in the dark-room.

To the clear filtrate a slight excess of dilute silver nitrate was added, precipitating the silver tribromothiophenolate as a white, gelatinous material. The silver salt was then washed repeatedly by digesting with water at 60° and filtering. This was repeated until the filtrate gave only a slight opalescence on adding dilute hydrochloric acid. The precipitate was finally drained on a fluted filter and allowed to dry in the air for thirty hours, carefully protected from dust. It was then dried in a vacuum desiccator over calcium chloride for a week.

This formed light-gray, very hard lumps which were crushed to a fine powder. The dried salt was kept in a desiccator in a dark-room, although it does not appear to be sensitive to light when dry. Heating to 80° in water causes considerable darkening. The product was not analyzed; however, the yields obtained in the following experiments indicated it to be quite pure.

Silver Tribromothiophenolate with One Equivalent of Iodine in Benzene.—Finely pulverized silver salt (7.4764 g.) was added to 2.091 g. of iodine in 50 cc. of dry benzene. The mixture was kept in a dark room for three days, with occasional shaking. The color of the iodine gradually disappeared. The solid was then filtered off and digested three times with warm benzene. The combined benzene filtrate and extracts were

[8] Leuckardt had obtained the analog of this dithiolcarbonate in the course of his preparation of thio-*p*-cresol, *J. prakt. Chem.*, [2] **41**, 189–191 (1890).

evaporated to about 4 cc. and cooled. Pale yellow crystals were deposited. The mother liquor was decanted and evaporated to dryness. This left 0.137 g. of a greenish-red oil. The crystalline product, which, as shown below, was 2,4,6,2′,4′,6′-hexabromodiphenyl disulfide, weighed 5.699 g., a yield of 92%.[9] The oily product was equivalent to 2.4% of the theoretical yield of disulfide.

That the oily product was not polydibromophenylene sulfide (the thio analog of the polydibromophenylene oxides discussed in the theoretical part) was shown by analysis.

Anal. Calcd. for $(C_6H_2Br_2S)_n$: Br, 60.10; S, 12.05. Found: Br, 50.12; S, 4.77.

The hexabromodiphenyl disulfide, a new compound, was further purified by washing with a small amount of ether and recrystallizing from benzene. It forms pale yellow rhombohedra, melting at 221.8–222.7° corrected. It is quite soluble in hot benzene or toluene, slightly soluble cold, very soluble in hot bromoform, ethylene dibromide, carbon disulfide or chloroform, fairly soluble cold. Ethyl acetate, glacial acetic acid or alcohol dissolve it only slightly.

The disulfide may be reduced to the thiophenol by treating the cold benzene solution, containing a few per cent. of alcohol, with granular sodium, keeping the mixture cool to avoid too vigorous reduction and removal of bromine from the ring. The sodium 2,4,6-tribromothiophenolate may be extracted easily with water and precipitated by acid.

The same disulfide is easily obtained by atmospheric oxidation of the ammonium or sodium salt of the thiophenol, by the action of halogen on the free thiophenol or its salts, or by the reduction of the salts of tribromobenzenesulfonic acid with phosphorus pentabromide.

Anal. (Carius at 300°) calcd. for $(C_6H_2Br_3S)_2$: Br, 69.32; S, 9.78. Found: Br, 69.49, 69.52; S, 9.78. Molecular weight calcd.: 692; found (cryoscopic, ethylene dibromide), 614.

2,4,6-$C_6H_2Br_3SAg$ with One-Tenth Equivalent of Iodine.—This experiment was carried out in the same way as the preceding one except that the reaction was completed in about thirty minutes, excess silver salt being present. The characteristic rhombohedron crystals of hexabromodiphenyl disulfide, identified by their melting point, were obtained; there was no oily or other by-product.

$C_6H_2Br_3SAg$ with One Equivalent of Iodine in Boiling Benzene.—The reaction was complete in thirty minutes. The product was hexabromodiphenyl disulfide and a trace of an oily by-product.

$C_6H_2Br_3SAg$ with Cold Ethyl Iodide.—To 1.994 g. of the dry, finely pulverized silver salt was added 15–20 cc. of dry, colorless ethyl iodide and the mixture kept in a darkened place for two days, when the reaction appeared to be complete. The silver iodide was filtered off and washed with ethyl iodide. Evaporation of the ethyl iodide left a viscous, light yellow oil which was freed of solvent by warming under vacuum and then drying in a desiccator.

The calculated yield was 1.649 g.; the actual yield was 1.655 g. or 100.3%. Analysis indicated the product to be pure ethyl tribromophenyl thio ether, $C_6H_2Br_3SC_2H_5$.

Anal. Calcd. for $C_8H_7Br_3S$: Br, 63.95; S, 8.55. Found: Br, 64.39, 64.02; S, 8.88, 9.04.

$C_6H_2Br_3SAg$ with Boiling Ethyl Iodide.—The same product was obtained as with cold ethyl iodide and in the same purity.

Anal. Calcd. for $C_8H_7Br_3S$: Br, 63.95; S, 8.55. Found: Br, 64.25; S, 8.86.

[9] This is not the same as the "hexabromodiphenyl disulfide" prepared by Taboury, *Bull. soc. chim.*, [4] **1**, 741 (1907).

$C_6H_2Br_3SAg$ at 110° with Ethyl Iodide.—About 2.0 g. of the silver salt was heated to 110° in an oil-bath and boiling ethyl iodide added; the silver salt was heated again up to 110° and another portion of hot ethyl iodide was added. The mixture was extracted with benzene and also chloroform but the only product obtained was the same light yellow, viscous oil produced with cold or hot ethyl iodide.

$C_6H_2Br_3SAg$ with Cold Methyl Iodide.—An excess of redistilled and dried methyl iodide was added to the finely pulverized, dry silver salt and the mixture allowed to stand in a darkened place for three days. The excess methyl iodide was filtered off and the solids washed with pure benzene. Evaporation of the combined extracts left long, colorless needles, plus about 1 or 2% of reddish oil which was not further investigated. The solid was recrystallized from hot alcohol or acetone and analyzed. It was methyl tribromophenyl thio ether (2,4,6-tribromothioanisole), $C_6H_2Br_3SCH_3$, crystallizing in long, flat, glistening, colorless needles, melting at 59.6–60.5°, very soluble in carbon bisulfide, acetone, chloroform, fairly soluble in glacial acetic acid, slightly soluble in ether or alcohol.

Anal. Calcd. for $C_7H_5Br_3S$: Br, 66.43; S, 8.88. Found: Br, 66.59; S, 9.12.

Effect of Heat upon $C_6H_2Br_3SAg$.—The dry salt heated in a test-tube immersed in an oil-bath at various temperatures from 120 to 180° for one hour suffered no detectable decomposition, as shown by extraction of the salt with chloroform, benzene, ether or carbon disulfide. The salt after these treatments was finally treated with iodine in benzene and gave the usual yield of hexabromodiphenyl disulfide in good purity.

2,4,6-$C_6H_2Br_3SNa$ with Bromine in Aqueous Potassium Bromide. Preparation of $C_6H_2Br_3SO_2Br$.—2,4,6-Tribromothiophenol (11.5 g.) was dissolved in a small excess of sodium hydroxide, the excess alkali nearly neutralized and then the mixture diluted to 150 cc., after which it was filtered in a very thin stream, with stirring, into a solution of 25 g. of bromine and about 20 g. of potassium bromide in 45 cc. of water. A reddish oil separated and solidified in a few minutes. The red-brown solid was washed with water several times by decantation and dried in the air.

The dried solid was extracted with ether several times. The insoluble portion was recrystallized from benzene and shown to be the 2,4,6,2′,4′,6′-hexabromodiphenyl disulfide obtained in the preceding experiments; yield about 45%.

The ether extracts were evaporated to dryness, the residues redissolved in the minimum amount of cold ether and filtered from the small amount of disulfide. From three crops of crystals was isolated 7.55 g. or nearly 50% yield of the sulfonyl bromide,[10] $C_6H_2Br_3SO_2Br$. Recrystallized from ether, m. p. 74.5–75.7°. It is exceedingly soluble in ether, benzene or chloroform. It forms the ethyl ester on boiling with alcohol. It is rapidly hydrolyzed to the sulfonate by warm alkali; it reacts violently with phosphorus tribromide, being almost instantly reduced to hexabromodiphenyl disulfide. Boiling with dilute acid for one hour hydrolyzed the product to hydrobromic acid, sulfuric acid and 1,3,5-tribromobenzene.

Anal. Calcd. for $C_6H_2Br_3SO_2Br$: Br, 69.85; S, 7.00. Found: Br, 69.70, 70.10; S, 6.86, 6.83.

2,4,6-$C_6H_2Br_3SNa$ with Liquid Bromine.—Treatment of about a gram of the sodium salt with liquid bromine gave rise to a rather violent reaction yielding a sticky red mass. This was extracted with chloroform but nothing was identified in the chloroform extract except the disulfide.

$C_6H_2Br_3SH$ with Bromine in Benzene.—To 20 cc. of dry benzene containing 1.2

[10] Michaelis and Ruhl prepared $C_6H_5SO_2Cl$ by analogous methods, *Ber.*, **23**, 475 (1890). This sulfonyl bromide is new although Reinke prepared the analogous sulfonyl chloride, $C_6H_2Br_3SO_2Cl$, *Ann.*, **186**, 277 (1877).

g. of the free thiophenol was added 0.3 cc. of bromine in 10 cc. of benzene and the mixture then allowed to stand for forty-eight hours. Evaporation of the benzene left yellowish granules and a little red oil. On exposure to the air the oil largely solidified. Although the product had first shown definite indications of the presence of considerable amounts of some other products, the procedure resulted in the ultimate identification of about 97% of the product as hexabromodiphenyl disulfide.

Product Formed by Bromine with Thiophenol in Glacial Acetic Acid.—Thiophenol (5.7 g.) was dissolved in 50 cc. of glacial acetic acid. To this was added 11.4 cc. of bromine and it was then allowed to stand for several hours, part of the time in sunlight. The solution was then cooled in an ice-bath, the solid filtered off, washed five times with cold acetic acid and then five times with water. After drying, the solid was recrystallized from alcohol; m. p. 91–93°. The melting point, crystalline form and analysis correspond to the 4,4′-dibromodiphenyl disulfide of Hübner and Alsberg.[11]

Anal. Calcd. for $(C_6H_4BrS)_2$: Br, 42.50. Found: Br, 42.87.

Summary

1. The salts of 2,4,6-tribromothiophenol, as well as the free thiophenol, react in a perfectly normal manner with halogens and alkyl halides to give the disulfide or thio ethers in nearly quantitative yield. The products contain nothing analogous to the amorphous polydihalogenophenylene oxides obtained from the trihalogenated phenols and phenolates.

2. The first stage in the reaction of both phenolates and thiophenolates is probably the formation of metal halide plus an unstable product containing halogen directly attached to oxygen or sulfur.

3. The first known member of the series of trihalogenated thiophenols has been prepared. From this eight derivatives have been prepared and characterized.

[11] Hübner and Alsberg, *Ann.*, **156**, 328 (1870).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

KETENES FROM ACYLPHTHALIMIDES AND OTHER SUBSTITUTED AMIDES

BY CHARLES D. HURD AND MALCOLM F. DULL

RECEIVED JANUARY 11, 1932 PUBLISHED JUNE 6, 1932

Acetylcarbazole is known[1] to regenerate carbazole on heating above its melting point. Propionylcarbazole,[2] *n*-nonoylcarbazole[3] and palmitylcarbazole show a similar instability on fusion. Although carbazole was identified in all cases, no attention was directed to the fate of the acyl radicals.

If the elements of carbazole, $(C_6H_4)_2NH$, are subtracted from those of acetylcarbazole, $(C_6H_4)_2NCOCH_3$, the elements of ketene remain. Whereas

[1] Graebe and Glaser, *Ann.*, **163**, 351 (1872).

[2] Oddo, *Mem. accad. Lincei*, [v] **14**, 510 (1923).

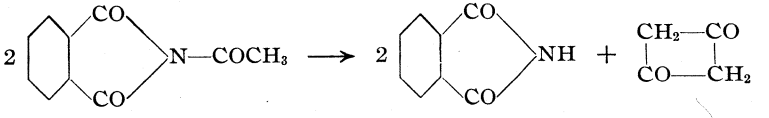
[3] Copisarow, *J. Chem. Soc.*, **113**, 816 (1918).

ketene was not found, its dimer was formed when dry acetylcarbazole was refluxed. Ketene dimer is considered[4] to be cyclobutanedione, $\begin{matrix} CH_2—CO \\ | \quad | \\ CO—CH_2 \end{matrix}$.

The ketene detachment from this acetyl derivative of carbazole was due, in part at least, to the weakness of carbazole as a base, since the acetyl derivative of ammonia, namely, acetamide, gave no incontrovertible evidence[5] of ketene as a product of pyrolysis. Therefore, other acyl derivatives of neutral or acidic trivalent nitrogen compounds were also tested for similar ketene production.

Acetyldiphenylamine, diacetamide and acetylphthalimide were taken. The first of these, despite its structural similarity to acetylcarbazole, was unchanged after 24 hours of refluxing (290°) or after passage through tubes at 500 or 600°. Diacetamide was less stable, giving good yields of acetic acid and acetonitrile[6] as it was passed rapidly through a tube at 635°. No evidence was obtained for ketene or its dimer: $(CH_3CO)_2NH \longrightarrow CH_3CN + CH_3CO_2H$.

Acetylphthalimide, previously described by Aschan[7] to be an active acetylating agent, was found to decompose at a refluxing temperature into phthalimide and to give remarkably good yields of ketene dimer, yields which were considerably better than from acetylcarbazole. This constitutes a very satisfactory new method for synthesizing ketene dimer



Although acetylphthalimide resembled acetylcarbazole in giving rise to ketene dimer, the former (when not especially dried) simultaneously produced acetic acid whereas the latter gave acetone. The acetic acid points to ketene as its precursor, whereas the acetone comes from the cyclobutanedione. Acetylphthalimide decomposed much more readily than acetylcarbazole, a fact which may explain why ketene exists for a moment in the first case but not in the second.

Ketenes from Other Acylphthalimides.—*n*-Propionyl-, *n*-butyryl- and *n*-caproyl-phthalimide were studied in the hope of obtaining, respectively, methylketene, ethylketene and *n*-butylketene or their dimers, but instead only decomposition products of these substances were isolated. *n*-Butyrylphthalimide, which was found to decompose spontaneously on keeping for a few hours, pyrolyzed into phthalimide, butyric anhydride,

[4] Chick and Wilsmore, *J. Chem. Soc.*, **97**, 1978 (1908); Staudinger and Bereza, *Ber.*, **42**, 4908 (1909).

[5] Hurd, Dull and Martin, THIS JOURNAL, **54**, 1974 (1932).

[6] The same products in a sealed tube experiment at 250° were reported by Hentschel, *Ber.*, **23**, 2396 (1890).

[7] Aschan, *ibid.*, **19**, 1398 (1886).

di-*n*-propyl ketone and carbon dioxide. The butyric anhydride is traceable through ethylketene and water whereas dipropylketone and carbon dioxide are traceable through the dimer of ethylketene and water. The source of such a quantity of water is not apparent for no more than traces should have been present. With acetylphthalimide which was dried in the same way as the butyrylphthalimide (air dried), some water was also present as evidenced by the production of acetic anhydride and acetone but even so, considerable ketene dimer was isolated as such.

Propionylphthalimide, which was purified and dried in such a way that water should have been completely excluded prior to its pyrolysis, behaved like the butyrylphthalimide. Propionic anhydride, diethyl ketone and carbon dioxide were formed between 220–320°. These products point to methylketene and its dimer as intermediates but neither could be isolated as such. Some water was even identified as such in the later stages of the pyrolysis. Its presence has no adequate explanation. Similarly, propionylcarbazole yielded distillation products which were analogous to those obtained from propionylphthalimide, namely, diethyl ketone and propionic anhydride.

Caproylphthalimide, on pyrolysis, gave rise to caproic acid and to an indifferent product which was a trimer of *n*-butylketene. Similar trimers were obtained by Wedekind[8] by the action of tertiary bases on acid chlorides.

***iso*-Butyrylphthalimide and Dimethylketene.**—When *iso*-butyrylphthalimide, $C_6H_4\begin{matrix}CO\\CO\end{matrix}NCOCH(CH_3)_2$, was heated to 225°, free dimethylketene was formed in substantial amounts. Even in its present state this method is considerably simpler than the existing method[9] for the synthesis of dimethylketene and, undoubtedly, the yield from the new method will be increased with further study.

Diphenylacetylphthalimide, $C_6H_4\begin{matrix}CO\\CO\end{matrix}NCOCH(C_6H_5)_2$, underwent pyrolysis into diphenylketene and phthalimide.

Comparison of the Methods with Existing Ones

Ketene Dimer.—At present this is best prepared by the slow polymerization of liquid ketene. Although gaseous ketene may be prepared easily from acetone, its liquefaction requires either solid carbon dioxide or liquid air temperatures, preferably the latter. Nothing of this nature is required in the preparation of ketene dimer from acetylphthalimide (or acetylcarbazole), for it is a direct product. Since acetylphthalimide may be prepared merely by refluxing phthalimide with acetic anhydride, the simplicity of the method is striking.

[8] Wedekind, *Ann.*, **323**, 246 (1902).

[9] Staudinger, *Ber.*, **39**, 968 (1908).

Dimethylketene.—To make an ether solution of dimethylketene, Staudinger[10] converted *iso*-butyric acid into α-bromo-*iso*-butyryl bromide, which, in ether solution, was dehalogenated with zinc. Ether and dimethylketene are inseparable by distillation. For pure dimethylketene, it was necessary to synthesize dimethylmalonic anhydride and to subject it to pyrolysis. It is obvious that the present method is simpler than either of these for *iso*-butyrylphthalimide is readily synthesized from *iso*-butyryl chloride and potassium phthalimide. From it, dimethylketene may be prepared without contamination by a solvent.

Diphenylketene.—The most satisfactory method for this preparation is the pyrolysis of azibenzil.[11] However, azibenzil is difficult to prepare, involving as it does the preparation of benzil hydrazone and dehydrogenation of the latter with mercuric oxide. In contrast, diphenylacetylphthalimide may be synthesized rapidly from diphenylacetyl chloride and potassium phthalimide. This compensates for the lower yield of diphenylketene which is obtained. It is believed that considerably better yields of diphenylketene and of dimethylketene may be developed with further study of the acylphthalimides.

Experimental Part

Preparation of Materials.—Acetyldiphenylamine[12] and acetylphthalimide[13] were prepared, respectively, in 88 and in 72–78% yields by literature methods. The former, crystallized from xylene and from alcohol, melted at 99°. Acetylphthalimide, after recrystallization from a hot benzene–petroleum ether solution, melted at 135–139° instead of 132–135° (Aschan's value).

Acetylcarbazole.—Graebe and Glaser[14] prepared this by heating acetic anhydride and carbazole in a sealed tube. With the following directions, developed in part by Mr. R. W. McNamee, the sealed tube was avoided.

Carbazole (200 g.) was refluxed with an excess of acetic anhydride (600 cc.) for twenty hours. This hot mixture was poured, with stirring, into one liter of water at 75°. The oily layer was separated, washed with sodium carbonate solution, with cold water till the mass solidified, and then crystallized from alcohol (500 cc. of alcohol for each 100 g. of acetylcarbazole). Decolorizing charcoal was used. The purified crystals were dried in air. They weighed 208 g. (83.3% yield) and melted at 69°.

Propionylcarbazole was also synthesized by refluxing for twenty-four hours 100 g. of carbazole and 300 cc. of propionic anhydride. The purification procedure was the same as with acetylcarbazole. An eighty gram (60%) yield of pure propionylcarbazole was isolated, m. p. 89.5°. Previously, Oddo[15] synthesized this compound from propionyl chloride and magnesium carbazole.

---

[10] Staudinger and Klever, *Ber.*, **39**, 968 (1908); Staudinger and Ott, *ibid.*, **41**, 2208 (1910).

[11] Schroeter, *ibid.*, **42**, 2345 (1909).

[12] Kaufmann, *ibid.*, **42**, 3480 (1909).

[13] Aschan, *ibid.*, **19**, 1398 (1886).

[14] Graebe and Glaser, *Ann.*, **163**, 351 (1872).

[15] Oddo, *Mem. accad. Lincei*, [v] **14**, 510 (1923).

Diacetamide.—Titherley's procedure[16] was modified. He suspended two moles of acetamide in benzene and treated it with one mole of acetyl chloride. We obtained better results by melting the acetamide (141 g.) and adding it slowly to 1.6 moles of a benzene (200–250 cc.) solution of acetyl chloride (100 g.) which was shaken constantly. Titherley's purification procedure was used. Yields were 35–45 g. (30–37%); m. p. 78–79°.

Propionylphthalimide.—A mixture of 100 g. of phthalimide and 250 cc. of propionic anhydride was refluxed for twelve hours. Crystals formed on cooling which were filtered off, dissolved in hot benzene and caused to crystallize by the admixture of petroleum ether. The fine yellow needles which were obtained in 72% yield (90 g.) melted at 143–144°.

Anal. (Kjeldahl) Subs., 0.2973, 0.3104: cc. of 0.2138 *N* acid, 6.90, 7.01. Calcd. for $C_{11}H_9O_3N$: N, 6.89. Found: N, 6.94, 6.76.

***n*-Butyrylphthalimide** was prepared by the interaction of 50 g. of potassium phthalimide and 45 g. of *n*-butyryl chloride in 450 cc. of dry benzene. Only at the start was warming required. When complete, it was filtered and worked up in a manner identical to that described below for caproylphthalimide. The yield of dry crystals was 23 g. or 39%. Even when freshly crystallized from alcohol or from ethyl acetate, the compound had a pronounced odor of butyric acid. The crystals softened at 70–72° but did not melt completely until the melting point of phthalimide was reached. On standing overnight in a corked bottle the crystals changed into an amorphous powder and acquired a pronounced acid odor.

Caproylphthalimide.—To a suspension of 25 g. of potassium phthalimide in 250 cc. of dry benzene there was added 25 g. of caproyl chloride. The solution was warmed to start the reaction, which completed itself in ten minutes. The potassium chloride was filtered off and the filtrate evaporated at room temperature. The dry residue was extracted for five minutes with 250 cc. of alcohol[17] at 30°. The solution was filtered rapidly by suction and the filtrate placed in a refrigerator until crystallization of the caproylphthalimide was complete, but not sufficiently long to permit separation of unchanged phthalimide. The large, lustrous, plate-like crystals were collected on a filter and air-dried; m. p. 78.5–79.5°; yield, 20 g. or 60%.

Anal. (Kjeldahl) Subs. 0.3177, 0.3097: cc. of 0.2138 *N* acid, 6.01, 6.00. Calcd. for $C_{14}H_{15}O_3N$: N, 5.72. Found: N, 5.77, 5.76.

Iso-butyrylphthalimide was prepared by the general procedure used for caproylphthalimide, taking 43 g. of potassium phthalimide, 50 g. of *iso*-butyryl chloride and 450 cc. of dry benzene. The product separated from alcohol in plate-like crystals; m. p. 96–98°; yield, 23 g. (45.7%).

Anal. (Kjeldahl) Subs. 0.3215, 0.3124: cc. of 0.2138 *N* acid, 6.96, 6.87. Calcd. for $C_{22}H_{11}O_3N$: N, 6.45. Found: N, 6.48, 6.58.

Diphenylacetylphthalimide.—The calculated quantity of diphenylacetyl chloride (23 g.) was refluxed vigorously for five minutes with a suspension of 18.5 g. of potassium phthalimide in 350 cc. of dry benzene. After filtering and evaporating to the consistency of a thin paste, petroleum ether was added and the whole chilled in a refrigerator for four hours. The crude crystals (13–15 g.) of diphenylacetylphthalimide thus pro-

[16] Titherley, *J. Chem. Soc.*, **79**, 411 (1901).

[17] In some cases alcohol cannot be used to extract or to crystallize the acylphthalimides because it is a reaction solvent. Then ethyl acetate may be used, but usually the compounds are too soluble in it for convenience. If ethyl acetate is used, it should be free from alcohol.

duced were contaminated with phthalimide. Purification was effected by crystallization from absolute ethyl acetate. Ordinary ethyl acetate gave trouble, probably due to its alcohol content. Diphenylacetylphthalimide melted at 170–171°. It was rather insoluble in cold alcohol; with warm alcohol it gave phthalimide and ethyl diphenylacetate.

Anal. Subs. 0.3111, 0.3009: cc. of 0.2138 *N* acid; 4.32, 4.36. Calcd. for $C_{22}H_{15}O_3N$: N, 4.14. Found: N, 4.16, 4.19.

Pyrolysis of Diacetamide.—Using the flow method previously described for acetamide,[18] diacetamide vapors were passed through a Pyrex tube (1.6 cm.) at 630–640°. An empty, ice-cold flask was placed between the furnace outlet and the aniline flask. Ketene was not formed since no acetanilide was found. With a 2.2 seconds contact time, 50 g. of diacetamide was passed during ten minutes. Only 1 g. was recovered; 27–27.5 g. of acetic acid and 18–19 g. of acetonitrile were formed. At 510° and 6.2 sec., at least one-third of the diacetamide remained unchanged.

Experiments with Acylphthalimides and Acylcarbazoles

General Procedure.—Quantities ranging from 15 to 75 g. of these amides were heated to gentle refluxing in a 125- or 250-cc. distilling flask, the side arm of which delivered into an empty 25-cc. distilling flask kept at 0°. The uncondensed vapors were conducted from this flask into a flask which contained 10 cc. of aniline.

Acetyl Derivatives

Acetylphthalimide started to decompose at 240° and at 284° the reaction became so vigorous that heating was stopped. Then heating was resumed up to 325° for one to four hours. In several runs, using 50 g., about 10 g. of distillate and only about 0.5 g. of acetanilide were identified. Consistently the distillate contained 3.5–4.5 g. (30–38% yield) of ketene dimer, b. p. 125–127°, and 5–5.5 g. of lower boiling material, three-fourths of which was acetic acid. The ketene dimer was identified by reaction with aniline, producing acetoacetanilide. The latter melted at 84°.

To remove traces of water (as evidenced by acetic acid formation) from the acetylphthalimide, 800 cc. of toluene was added to 150 g. of the material and 200 cc. of the toluene distilled from it at 20 mm. One liter of petroleum ether was poured into the residual solution and the precipitated acetylphthalimide filtered by suction in an atmosphere of dry air. Heating 70 g. of this material for an hour or 50 g. for five hours gave, respectively, 9.2 and 8.7 g. of pure ketene dimer. These values represent 53 and 75% of the theoretical. Only traces of acetic acid were produced.

Acetylcarbazole.—This material started to decompose at 200°, the temperature gradually increasing to 356°. Heating 75 g. for six to seven hours gave 3–3.1 g. of ketene dimer (b. p. 125–127°, and yielding acetoacetanilide with aniline) and 1–1.2 g. of acetone (b. p. 56–57°, and yielding benzylideneacetone, m. p. 111–112°, with benzaldehyde). There was no acetanilide and little or no acetic acid. The yield of ketene dimer was 20%.

When 75 g. of acetylcarbazole was heated at 110° and 15 mm. for three hours to dry it, subsequent pyrolysis for three hours gave rise to a 5.6 g. (37%) yield of ketene dimer and only 0.1 g. of acetone.

Acetyldiphenylamine.—When 75 g. of this amide was refluxed for twenty-four hours, only a few drops of distillate were collected. The amide changed in part to a black tar, but much was recoverable. No ketene or ketene dimer appeared. Following this, 50 g. was passed during twelve to fifteen minutes through a Pyrex combustion

[18] Hurd, Dull and Martin, THIS JOURNAL, **54**, 1974 (1932).

tube at 500 or at 600° with a recovery of 45–46 g. of the original amide. Apparently no ketene was formed nor was ammonia evolved. Some charring was observed.

Propionyl Derivatives

Propionylphthalimide.—This compound started to decompose at 220°, the temperature gradually being increased to 322°. The heating was maintained for three hours, but most of it was completed in thirty minutes. Besides phthalimide, the reaction products were diethyl ketone and propionic anhydride, equal weights of the last two substances being formed. After one and one-half hours, droplets of water appeared in the side arm of the condensing flask. This water was characterized by its melting point and by its ability to dissolve anhydrous copper sulfate to a blue solution. In a series of pyrolyses using 15-g. portions, there was formed 1.2–1.5 g. of diethyl ketone (38–47% yield) and 1.2–1.4 g. (25–29%) of propionic anhydride. The ketone was collected by distillation at 101–104° and was identified as 2,6-diphenyl-3,5-dimethyltetrahydro-γ-pyrone,[19] m. p. 106°, its reaction product with benzaldehyde and alcoholic potassium hydroxide. The distillate collected between 160–170° was considered to be propionic anhydride since it was neutral to litmus but dissolved slowly in water to give an acid reaction. It gave propionanilide by reaction with aniline and it analyzed as an acid anhydride.

Analysis of Propionic Anhydride.—Whitford[20] showed that acetic anhydride reacted quantitatively with anhydrous oxalic acid and dry pyridine to evolve carbon monoxide and carbon dioxide. We found that the method was also adaptable for the quantitative determination of propionic anhydride. With pure propionic anhydride a 100% value was established

$$(C_2H_5CO)_2O + (CO_2H)_2 \xrightarrow{\text{pyridine}} 2C_2H_5CO_2H + CO + CO_2$$

Using this method of analysis on the total distillate (8.3 g.) from a 50-g. sample, 21% of propionic anhydride or 1.24 g. was established whereas in the run under consideration, 2.0 g. of distillate was found between 160–178°.

Manner of Drying.—In these experiments the propionylphthalimide was dried in several ways without materially changing the result. Thus, 50 cc. of benzene or 50 cc. of toluene or 50 cc. of xylene was distilled from the 15-g. sample using diminished pressures so that distillation temperatures, respectively, of 40, 75 and 100° were attained. All water was undoubtedly removed by this method, but, as stated above, water was formed during the pyrolysis. Hence, neither methylketene or its polymer were isolated as such. In other similar experiments, propionylphthalimide was dried by heating it in an oven for four hours at 105° before use.

Gas Formed.—In one experiment on a 50-g. sample, 12.3 liters (standard conditions) of gas was collected. Analysis showed 81.9% of CO_2, 6.7% CO, the remainder being nitrogen. This represents 2.0 g. of carbon dioxide, which is equivalent to 3.9 g. of diethyl ketone; actually 2.9 g. of distillate was collected between 101–104°.

Propionylcarbazole.—Decomposition of a 40-g. sample started at 240° and the temperature was increased to 361°. After four hours, 5.1 g. of liquid had distilled. Carbon dioxide was evolved during the pyrolysis. The distillate was very similar to the one from propionylphthalimide and consisted of diethyl ketone and propionic anhydride.

***n*-Butyrylphthalimide.**—Fifteen grams of air-dried material was heated in the usual way. It yielded 3.6 g. of distillate, which contained 1.7 g. of dipropyl ketone

[19] Vorländer and Hobohm, *Ber.*, **29**, 1352 (1896).

[20] Whitford, THIS JOURNAL, **47**, 2939 (1925).

(b. p. 143–147°), 0.2 g. of butyric acid (b. p. 147–188°), and 1.4 g. of butyric anhydride (b. p. 188–195°).

Caproylphthalimide.—The following is a typical run out of several which were performed. Caproylphthalimide was recrystallized from ethyl acetate and dried in a vacuum desiccator over sulfuric acid for four days or longer. Pyrolysis of 25 g. of it (140–230°) during twenty minutes yielded about half a liter of carbon dioxide. The distillate contained phthalimide and caproic acid, separation of these two being effected by solution of both in petroleum ether and precipitation of phthalimide from the solution at 0°. Distillation of the petroleum ether filtrate yielded 1.8 g. of caproic acid at 200–210°. Its potassium salt was obtained readily by the action of potassium hydroxide solution. Evaporation of the water, extraction of the potassium caproate in hot alcohol, cooling, filtering and washing with ether gave the salt in a pure state.

Anal. Calcd. for $C_5H_{11}CO_2K$: K, 25.03. Found: K, 25.06.

The non-volatile product in the original reaction flask was extracted while still molten with 100 cc. of petroleum ether. Whatever crystals formed on cooling this solution by ice were removed, after which the hydrocarbon was distilled off, leaving 8–9 g. of an oil. When distilled, besides a tarry residue, there was about 3 g. of an oil which was collected at 213–216° (5 mm.). Its molecular weight and analysis designated it to be *n*-butylketene trimer.

Anal. Subs. 0.2247: CO_2, 0.6045; H_2O, 0.2058. Calcd. for $(C_4H_9CH{=}C{=}O)_3$: C, 73.41; H, 10.28. Found: C, 73.34; H, 10.24.

Mol. wt. Subs. 0.2201, 0.3154; benzene, 21.975 g.; f. p. lowering, 0.159, 0.223°. Calcd. for $C_{18}H_{30}O_3$: mol. wt., 294. Found: mol. wt., 322, 329.

This polymer was neutral, insoluble in dilute acids and soluble in concentrated sulfuric acid. It did not react with aniline or with bromine. Reaction evidently was possible with alkali, for on long standing with dilute sodium hydroxide solution the oil dissolved.

It was established that only 6 g. out of 50 of caproylphthalimide was recoverable after twenty minutes of heating at 145–150°.

Iso-butyrylphthalimide.—Thirty grams of the pure *iso*-butyrylphthalimide, which had been recrystallized from ethyl acetate and dried *in vacuo* over sulfuric acid for several days, was heated for thirty minutes in an atmosphere of nitrogen. Decomposition began at 225°. The products of the reaction were passed into a flask which contained ice-cold absolute ether and the unabsorbed gases conducted into aniline. A white solid which remained in the side arm of the reaction flask was scraped into the ether at the end of the heating.

This ether solution was bright yellow in color due to dimethylketene.[21] In one experiment this color did not disappear completely on standing for three days but in another it disappeared in twenty-four hours due to polymerization to the colorless dimer. Evaporation of the ether left a residue of 2.5 g. of dimethylketene dimer (tetramethylcyclobutanedione) which possessed the characteristic camphor-like odor and which melted at 111–114°. From the aniline, 0.9 g. of *iso*-butyranilide was isolated. The dimethylketene which is thus indicated from *iso*-butyrylphthalimide is 30% of the theoretical.

Diphenylacetylphthalimide.—After remaining for two weeks in a vacuum desiccator over sulfuric acid, 20 g. of diphenylacetylphthalimide was pyrolyzed in a nitrogen atmosphere for twenty minutes. Decomposition was between 300–325°. There was

[21] For the isolation of pure dimethylketene, the ether trap would be replaced by an empty receiver kept at a sufficiently low temperature for liquefaction, a temperature of −78° favoring non-polymerization.

no distillate. The material in the flask was extracted thrice with 50-cc. portions of hot petroleum ether. About 9 g. of phthalimide resisted solution. After removal of the petroleum ether, 10 g. of a dark red oil remained from which 1.2 g. of diphenylketene distilled at 146–150° (14 mm.) and 6 g. between 150–240°. The latter was a red oil which slowly hardened to a glass. This was shown to contain phthalimide and a dimer of diphenyl ketene.

The diphenylketene was characterized by its vigorous reaction with aniline, giving diphenylacetanilide, m. p. 180°, by its yellow color and sharp, aromatic odor, and by its change into a colorless peroxide on standing in the air.

The 6 g. of higher boiling distillate was worked up by dissolving it in 25 cc. of hot alcohol. Phthalimide, m. p. 225–226°, separated on cooling to room temperature. It was filtered off and the filtrate cooled to 0°. A dark red, semi-crystalline mass separated which was filtered by suction and pressed out on a clay plate. Under these conditions, it gradually became almost clear white. When dry, the melting point was 188–190°, which is the melting point given by Staudinger[22] for a dimer of diphenylketene. About 1.7 g. of this substance was obtained.

Repetition of the experiment gave 0.9 g. of diphenylketene and 2.1 g. of the dimer.

Summary

Both acetylphthalimide and N-acetylcarbazole undergo decomposition at refluxing temperatures into cyclobutanedione, the dimer of ketene. *Iso*-butyrylphthalimide and diphenylacetylphthalimide undergo a similar pyrolysis into dimethylketene and diphenylketene. These reactions are suitable for synthetic work.

Propionylphthalimide, propionylcarbazole, *n*-butyrylphthalimide, and caproylphthalimide gave reaction products which pointed to the ketenes as intermediate products but these monoalkylketenes could not be isolated as such. Acetyldiphenylamine and diacetamide were also investigated. All of these acylphthalimides except acetylphthalimide are new compounds. The trimer of butylketene was identified as a product of the pyrolysis of caproylphthalimide.

EVANSTON, ILLINOIS

[22] Staudinger, *Ber.*, **38**, 1735 (1905); *Ann.*, **356**, 51 (1907).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A NEW REDUCTION OF ARYL SULFONIC ACID SALTS AND DERIVATIVES. PHOSPHORUS PENTABROMIDE AS A REDUCING AGENT[1]

BY ARTHUR H. KOHLHASE[2]

RECEIVED JANUARY 15, 1932 PUBLISHED JUNE 6, 1932

By the action of a strong aqueous solution of bromine and potassium bromide upon the sodium salt of 2,4,6-tribromothiophenol,[3] a new compound, tribromobenzenesulfonyl bromide, was obtained. We sought, for purposes of identification, to prepare this compound by heating potassium 2,4,6-tribromobenzenesulfonate with phosphorus pentabromide. However, the only product obtained was 2,4,6,2′,4′,6′-hexabromodiphenyl disulfide. This efficient reduction by pentavalent phosphorus was very puzzling, and led to the investigation described in this paper.

The following equations are now believed to represent the course of the reaction

$$RSO_3Na + PBr_5 \longrightarrow RSO_2Br + NaBr + POBr_3 \quad (1)$$

$$PBr_5 \rightleftharpoons PBr_3 + Br_2 \quad (2)$$

$$2RSO_2Br + 5PBr_3 \longrightarrow RSSR + 4POBr_3 + PBr_5 \quad (3)$$

The relative speeds of reactions (1) and (3) should be dependent on the nature of the aryl radical, R, and it was found that by varying R the reaction could be made to give almost exclusively the sulfonyl bromide, or varying proportions of the sulfonyl bromide and disulfide, or only the disulfide.

This mechanism would lead one to expect that the intermediate sulfonyl bromide would be reduced by phosphorus pentabromide and, more readily, by phosphorus tribromide. Furthermore, in those cases where no RSO_2Br could be found in the final reaction product it would be expected that the sulfonyl bromide would be rapidly reduced by phosphorus tribromide. As shown in Table I, the results fully confirmed this theory.

That *phosphorus pentabromide is essential for the first step* in the production of disulfides from sulfonic acid salts as indicated in reaction (1) was shown by heating some of the sodium sulfonate with phosphorus tribromide; neither the disulfide nor the sulfonyl bromide was formed in detectable amounts.

It is well known that phosphorus pentabromide dissociates very readily[4]

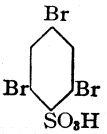
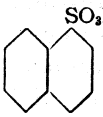
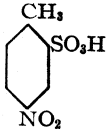
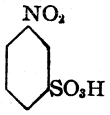
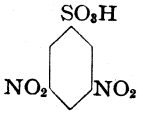
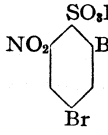
[1] This article is based upon Part I of a thesis presented by Arthur H. Kohlhase to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1924. The work was carried out under the direction of the late Professor W. H. Hunter.—L. I. SMITH.

[2] Present address, 1114 North First St., Phoenix, Arizona.

[3] Hunter and Kohlhase, THIS JOURNAL, **54**, 2425 (1932).

[4] Kastle and Beatty, *Am. Chem. J.*, **21**, 392–398 (1899).

TABLE I

Sulfonic acid	Derivative[a]	Reducing agent	Time of heating, min.	Products[a]	Yield,[c] %
	ASO_3Na[e]	PBr_5[b]	5–10	ASSA	86.5
	ASO_3Na	PBr_5	5–10	ASSA	9–35.7
	ASO_3Na	PBr_3	10	..	0
	ASO_2Br	PBr_3	0	ASSA	91.5
	ASO_2Br	PBr_5	25	ASSA	60.6
	ASO_3Na	PCl_5	20	ASO_2Cl, ASSA	97 0
	ASO_2Br	PCl_3	10	..	0
	ASO_2Cl	PBr_3	25	ASSA	34
	BSO_2Cl	PBr_3	25	..	0
	BSO_2Br	PBr_3	15	BSSB	28.7
				BSH	19.5
	CSO_2Cl	PBr_3	30	CSSC[e]	85.7
	DSO_3Na	PBr_5	30	DSO_2Br	45
				DSSD	3
	DSO_3Na	$PBr_5 + PBr_3$	15	DSO_2Br	*Ca.* 20
				DSSD	*Ca.* 40
	ESO_3Na	PBr_5	70	ESO_2Br, ESSE	*Ca.* 25 27.4
	ESO_3Na	$PBr_5 + PBr_3$	70	ESO_2Br, ESSE	0 57
	FSO_3Na	PBr_5	40	..	0
	$(FSO_3)_2Ba$	PCl_5	40	FSO_2Cl	84
	FSO_2Cl	PBr_3	40	FSSF[e]	*Ca.* 60
	$FSO_2SC_6H_5$[e]	PBr_3	0	FSH[e] (FSSF)[e]	*Ca.* 85–95
	GSO_3Na	PBr_5 at 100°	20	?	1–3
	GSO_3Na	PBr_5 at 150°	60	(?)[d]	

[a] The letters A, B, C, etc., used in these columns stand for the aryl radical of the parent sulfonic acids shown in the first column.

[b] This was a comparatively crude phosphorus pentabromide prepared in carbon bisulfide; all the remaining experiments were carried out with pure phosphorus bromides or chlorides prepared in carbon tetrachloride.

[c] The yield depended to a large extent upon keeping the products thoroughly mixed and also on the rate of heating.

[d] Reaction evidently occurred but the products could not be identified.

[e] A new compound.

according to reaction (2) and that the pentachloride behaves similarly at somewhat higher temperatures. However, when sodium 2,4,6-tribromobenzenesulfonate was treated with phosphorus pentachloride, it gave a 97% yield of the sulfonyl chloride and no detectable quantity of hexabromodiphenyl disulfide.[5]

Even when the sulfonyl bromide was prepared and then heated with phosphorus trichloride, there was no reduction, in marked contrast to the action of the tribromide. As illustrated in Table I by the sulfonyl bromides and chlorides of tribromobenzene and naphthalene, the substitution of chlorine for bromine in the sulfonyl halide also results in an increased resistance to reduction by phosphorus tribromide.

Reactions (1) and (3) may be combined

$$2RSO_3Na + 6PBr_5 \longrightarrow RSSR + 6POBr_3 + 2NaBr + 5Br_2 \quad (4)$$
$$2RSO_3Na + 6PCl_5 \longrightarrow RSSR + 6POCl_3 + 2NaCl + 5Cl_2 \quad (5)$$

By subtracting these two equations, taking account of the heats of formation of each substance,[6] we obtain the interesting result that reaction (5) is the more exothermic, in the case of *all* sulfonic acids, by 34,000 cal. Yet reaction (5) does not take place at all while reaction (4) proceeds with varying ease, depending on the nature of R. Very similar results are obtained in the case of reaction (3) and its analog.

It is significant that, although the oxidations of the tribromide and trichloride of phosphorus occur with nearly the same heats of reaction, there is other evidence that the tribromide is oxidized far more *readily*.[7]

One disulfoxide (phenyl-3,5-dinitrobenzene thiosulfonate) was treated with phosphorus tribromide, and reacted with surprising ease to give 3,5-dinitrothiophenol. The 3,5-dinitrodiphenyl disulfide would have been expected but it has been shown[8] that such unsymmetrical disulfides tend to rearrange to the symmetrical ones.

The production of 3,5-dinitrothiophenol instead of the corresponding disulfide was observed also in the case of α-naphthalenesulfonyl bromide. The final stage of the reduction is probably due to phosphorous acid. Some of these sulfonates have previously been treated with phosphorus pentabromide but the reductions here described were apparently not observed.[9]

This new method is very convenient for the preparation of disulfides which would otherwise be difficult to synthesize, even by the method of

[5] Reinke, *Ann.*, **186**, 271 (1877); Knuth, *ibid.*, **186**, 284 (1877).

[6] The data used were taken from Gmelin-Kraut, "Handbuch der anorg. Chemie," and are due to Thomsen, Berthelot and Ogier.

[7] Demole, *Ber.*, **13**, 1980 (1880); *Jahresb.*, 384 (1880); Michaelis, *ibid.*, 280 (1870).

[8] Lecher, *Ber.*, **53**, 591 (1920); Smiles and Gibson, *J. Chem. Soc.*, **125**, 176 (1924); but *cf.* also Smiles and McClelland, *ibid.*, **121**, 86 (1922).

[9] Limpricht, *Ann.*, **278**, 246 (1894); Forsling, *Ber.*, **22**, 1402 (1899).

Leuckardt.[10] These disulfides may in turn be converted to the corresponding thiophenols by reduction or by treatment with potassium sulfide.[11]

Experimental Part

I. Preparation of Sodium 2,4,6-Tribromobenzenesulfonate, $C_6H_2Br_3SO_3Na\cdot 1.5H_2O$.—Redistilled 1,3,5-tribromobenzene (one degree boiling range) was sulfonated by the method of Bössmann.[12]

The sodium tribromobenzenesulfonate obtained was recrystallized from the minimum amount of boiling water. It formed pure white flakes, readily soluble in hot water, only slightly soluble in cold. The sodium salt has not been previously described.

Anal. Calcd. for $C_6H_2Br_3SO_3Na\cdot 1.5H_2O$: H_2O, 6.08; SO_3, 19.20; Br, 57.52. Found: H_2O, 6.09; SO_3, 18.14; Br, 57.25, 57.96.

II. Reaction between Sodium 2,4,6-Tribromobenzenesulfonate and Phosphorus Pentabromide.—Two grams of the pure, anhydrous sodium salt was intimately mixed with 6.4 g. of phosphorus pentabromide and gently heated to 80–90° above a small flame with repeated remixing until the reaction started and rapidly spread throughout the mass; then about five minutes longer.

The reaction product was extracted twice with 20 cc. of dry, boiling benzene; these extracts were evaporated to a small volume and cooled. The yield of crystals was increased by diluting the oily mixture of benzene and phosphorus oxybromide with ether. The solvent was poured off and the crystals were washed with ether and then recrystallized from boiling benzene. Pale yellow rhombohedra separated, identical in form, color and solubility with 2,4,6,2′,4′,6-hexabromodiphenyl disulfide prepared by other methods;[3] yield, 13–38%; m. p. 218–218.5°, mixed m. p. 218–218.5°; 40–60% of the original sodium salt was recovered. An 86.5% yield of the disulfide was obtained when crude phosphorus pentabromide was used.

Evaporation of the ether washings left a sirupy oil which proved to be phosphorus oxybromide. No tribromobenzenesulfonyl bromide could be found.

III. Reaction between Sodium 2,4,6-Tribromobenzenesulfonate and Phosphorus Tribromide.—Two grams of the anhydrous sodium salt, heated for ten minutes at 90° with 4.0 g. of phosphorus tribromide gave no disulfide, sulfonyl bromide or thiophenol. The mixture left after ether extraction was completely soluble in water. After neutralization and recrystallization 92% of the original sodium salt was recovered.

IV. Reaction between 2,4,6-Tribromobenzenesulfonyl Bromide and Phosphorus Tribromide.—Phosphorus tribromide was added in excess to 1.0 g. of the sulfonyl bromide. The temperature quickly rose to about 175° and the reaction was completed in about two seconds. Ether was added to the cooled mixture which was then carefully treated with 23 cc. of water. The disulfide was recrystallized from benzene; yield, 0.691 g. or 91.5%.

V. Reaction between 2,4,6-Tribromobenzenesulfonyl Bromide and Phosphorus Pentabromide.—An intimate mixture of the reactants was heated for twenty-five minutes at 85–90°. The cooled product was treated with ether and then excess water, causing the separation of disulfide. The ether layer was washed with water and evaporated, leaving the 2,4,6-tribromobenzenesulfonyl bromide; recovery, 17%. The hexabromodiphenyl disulfide was filtered from the water layer, washed with water and ether; yield, 60.6%.

VI. Reaction between Sodium 2,4,6-Tribromobenzenesulfonate and Phosphorus

[10] Leuckardt, *J. prakt. Chem.*, [2] **41**, 179–224 (1890).

[11] Otto and Rössing, *Ber.*, **19**, 3129 (1886).

[12] Bössmann, *Ann.*, **191**, 206 (1878).

Pentachloride.—The reaction was carried out as in II and III, with the addition of four drops of phosphorus oxybromide. No disulfide was formed; yield of sulfonyl chloride, 97%.

VII. Reaction between 2,4,6-Tribromobenzenesulfonyl Bromide and Phosphorus Trichloride.—This was carried out as in experiment IV. No reduction occurred.

VIII. Reaction between 2,4,6-Tribromobenzenesulfonyl Chloride and Phosphorus Tribromide.—The reactants when mixed became *colder*. After heating in a bath at 80–85° for twenty-five minutes, the product was isolated as in V; yield of disulfide, 34%. A large portion of the original sulfonyl chloride was recovered unchanged.

IX. Reaction between α-Naphthalenesulfonyl Chloride and Phosphorus Tribromide.—The mixture was treated as in experiment X, but the naphthalenesulfonyl chloride was unchanged.

X. Reaction between α-Naphthalenesulfonyl Bromide and Phosphorus Tribromide.—Two grams of the sulfonyl bromide was warmed at 70° for fifteen minutes with 3.0 g. of phosphorus tribromide; the cooled mixture was dissolved in 15 cc. of ether, filtered and treated dropwise with 5 cc. of water. The sirupy solution, which had begun to deposit crystals, was further diluted until a cloudiness just developed and then cooled to 0°. The crystals were washed with water and dried; yield, 28.7%; m. p. 86.3–88.5°; mixed m. p. 87–88.5°. The known disulfide alone melted at 88–89.5°.[13]

The filtrate was diluted with excess water, the ether layer was separated and the water was extracted twice with ether. Evaporation of the ether extracts left an oil which was dissolved in ammonia water and oxidized in the air for twelve days, with occasional shaking. The white precipitate was recrystallized from alcohol; m. p. and mixed m. p. proved it to be α-naphthyl disulfide; yield, 19.5%.

Anal. Calcd. for $C_{20}H_{14}S_2$: S, 20.14. Found: S, 20.77.

XI. Reaction between 3-Nitro-6-methylbenzenesulfonyl Chloride and Phosphorus Tribromide.—Four grams of the sulfonyl chloride was heated with 14.4 g. of phosphorus tribromide at 75° for thirty minutes. The cooled mixture was dissolved in 15 cc. of ether. The clear solution was carefully treated with 8.5 cc. of water and cooled to 0°. The small needles, recrystallized from alcohol, melted at 147.3–148°; yield, 2.455 g. or 85.7%.

This disulfide is new. It crystallizes from alcohol in long, silky, white needles. It is soluble with difficulty in hot alcohol, more readily in hot glacial acetic acid, fairly soluble in ether, very soluble in benzene; it is insoluble in cold alkalies or dilute mineral acids. Analysis and its method of synthesis indicated it to be 3,3′-dinitro-6,6′-dimethyl diphenyl disulfide.

Anal. Calcd. for $C_{14}H_{12}O_4N_2S_2$: S, 19.07; N, 8.33; NO_2, 27.35. Found: S, 19.20, 18.61; N, 8.74; NO_2 (English),[14] 26.84.

It is worthy of notice that, while the sulfonyl chloride group was reduced, the nitro group was unaffected.

XII. Reaction between Sodium Benzenesulfonate and Phosphorus Pentabromide.—The sodium benzenesulfonate contained 38.7% of sodium chloride; 3.60 g. (equivalent to 2.21 g. of pure sodium benzene sulfonate) was mixed with 30 g. of phosphorus pentabromide and heated at 85–90° for thirty minutes. The cooled mixture was digested twice with absolute ether; 40 cc. of 15% sodium hydroxide was added *slowly* to the ether and then sodium carbonate till nearly neutral. The ether layer was separated and the water layer was extracted twice with ether. The combined extracts were evaporated.

[13] Schertel, *Ann.*, **132**, 91 (1864), gives m. p. 85°; Leuckardt, *J. prakt. Chem.*, [2] **41**, 217 (1890), gives m. p. 91°.

[14] English, *J. Ind. Eng. Chem.*, **12**, 994 (1920).

The oily, semi-solid residue was digested with 10 cc. of hot, saturated ammonia water for fifteen minutes, diluted with water to 35 cc., heated to 80° and decanted, removing the sulfonyl bromide as the sulfonamide. A few drops of oil were left.

The sulfonamide solution was evaporated to 25 cc. and cooled, depositing 0.90 g., 47% of the sulfonamide.

The few drops of oil left after the extraction with ammonia water were extracted with ether; the ether was evaporated and the residue was boiled with 1.5 cc. of alcohol and decanted. A small amount of oil separated from the cooled alcohol. The alcohol was poured off and cooled in an ice-bath, depositing a few white needles. Recrystallized from 0.6 cc. of alcohol, these melted at 58–59°; mixed m. p. with known diphenyl disulfide, 58–60°; yield, 0.04 g. or 3%.

XIII. Reaction between Sodium Benzenesulfonate and Phosphorus Pentabromide and Tribromide.—The sodium benzenesulfonate, 3.60 g., containing 1.39 g. of sodium chloride, was heated with 20 g. of phosphorus pentabromide and 13.5 g. of the tribromide for fifteen minutes at 85–90°. The products were isolated substantially as in experiment XII: approximately 20 and 40% yields of the sulfonyl bromide and diphenyl disulfide, respectively; m. p. of disulfide 59.5–61.5°; mixed m. p. showed no depression.

Anal. Calcd. for $C_6H_5SSC_6H_5$: S, 29.38. Found: S, 29.99.

XIV. Reaction between Sodium *m*-Nitrobenzenesulfonate and Phosphorus Pentabromide.—The sulfonate used contained 4.2% sodium carbonate and 59.7% of sodium sulfate. This mixture, 4.5 g., was heated with 29 g. of phosphorus pentabromide at 85–100° for seventy minutes. Isolation of the products as in experiment XII gave about a 25% yield of the sulfonyl bromide (determined as the sulfonamide, m. p. 160.5–162.5°)[15] and 0.30 g. or 27.4% yield of 3,3′-dinitrodiphenyl disulfide; m. p. 82–83°, recrystallized from ether.[16]

Anal. Calcd. for $C_6H_4NO_2SSC_6H_4NO_2$: S, 20.80. Found: S, 20.51, 21.44.

XV. Reaction between Sodium *m*-Nitrobenzenesulfonate and Phosphorus Pentabromide and Tribromide.—Four and five-tenths grams of the impure sodium salt (see XIV) was heated with 10 g. of phosphorus pentabromide and 14 g. of tribromide at 85–90° for seventy minutes. No sulfonyl bromide was found. The recrystallized disulfide melted at 81.2–82.2°; yield, 0.64 g. or 57.6%.

XVI. Reaction between 3,5-Dinitrobenzenesulfonyl Chloride and Phosphorus Tribromide.—Sodium 3,5-dinitrobenzenesulfonate could not be induced to react with phosphorus pentabromide. Accordingly, 2.00 g. of the sulfonyl chloride was heated with 2.5 cc. of phosphorus tribromide at 100–110° for forty minutes.

Treatment with ether and water, as in previous experiments, caused the separation of unchanged sulfonyl chloride. The filtrate was diluted with water until about to form two layers and cooled to 0°, giving 60% of the calculated quantity of 3,5,3′,5′-tetranitrodiphenyl disulfide, a new substance.

Anal. Calcd. for $C_6H_3(NO_2)_2SSC_6H_3(NO_2)_2$: S, 16.10. Found: S, 15.99.

This disulfide crystallizes from benzene on careful dilution with ligroin or ether in small pale yellow crystals, m. p. 175–177.5°. It is about as soluble in cold as in hot solvents, quite soluble in chloroform, fairly soluble in glacial acetic acid, very slightly soluble in ether, ligroin, or alcohol. Heated well above the melting point, it puffs and chars.

Preparation of Phenyl 3,5-Dinitrobenzenethiosulfonate, and Unsymmetrical Disulfoxide.—One mole of 3,5-dinitrobenzenesulfonyl chloride dissolved in benzene was added slowly to a suspension of two moles of anhydrous sodium thiophenolate in benzene. The mixture was thoroughly digested and then stoppered tightly for one hour.

[15] Limpricht, *Ann.*, **177**, 71 (1875), gives m. p. 161°.

[16] Cleve, *Ber.*, **20**, 1534 (1887), gives m. p. 83°.

The solids were filtered off, washed with benzene, again suspended in benzene and treated with a benzene solution of bromine until the bromine color persisted. The solution was filtered and evaporated *in vacuo* at 105° to an oily residue which was then exposed on a watch glass, finally giving a partially crystalline mass consisting of two substances: A, exceedingly soluble (not identified but probably diphenyl disulfide), and B, slightly soluble in ether.

Substance A was separated by ether and B was recrystallized twice from benzene and once from alcohol. It was phenyl 3,5-dinitrobenzenethiosulfonate, a new compound. It crystallizes from alcohol as pale yellow needles, m. p. 139–141°. It is very soluble in benzene, fairly soluble in hot alcohol, slightly soluble in ether. The disulfoxide group is very readily reduced by phosphorus tribromide.

Anal. Calcd. for $C_6H_3(NO_2)_2SO_2SC_6H_5$: S, 18.84. Found: S, 19.43.

This disulfoxide gives sodium thiophenolate and sodium dinitrobenzenethiosulfonate when treated with sodium sulfide.[17] The thiophenolate was identified as the disulfide, m. p. 59–60°, mixed m. p. 60.5–61.5°. This proved the presence of a C_6H_5S-group in the disulfoxide. The presence of a $C_6H_3(NO_2)_2SO_2$– group was shown by experiment XVII.

XVII. Reaction between Phenyl 3,5-Dinitrobenzenethiosulfonate and Phosphorus Tribromide.—To 0.95 g. of phenyl 3,5-dinitrobenzenethiosulfonate was added 1 cc. of cold phosphorus tribromide. The temperature quickly rose to the boiling point and in about two seconds the reaction was over; 15 cc. of ether was added to the cooled mixture and then 40 cc. of water.

The water layer was neutralized with sodium carbonate, then 4 cc. of ammonia water was added and the mixture was allowed to oxidize in the air. The brown, tarry precipitate formed during the first twenty-four hours was discarded. The succeeding precipitate was filtered after one week and recrystallized from benzene and ligroin. It was shown to be 3,5,3′,5′-tetranitrodiphenyl disulfide (see experiment XVI), m. p. 175–177.5°; yield, 85–95%.

Preparation of 2,4-Dibromo-6-nitrobenzenesulfonic Acid.—Blanksma's preparation of the corresponding disulfide by the use of sodium disulfide[18] suggested that this sulfonic acid might be prepared by the interaction of sodium sulfite and 1,2-dinitro-3,5-dibromobenzene.[19]

Ten grams of dinitrodibromobenzene was dissolved in 100 cc. of hot 95% alcohol. To this was added 4.63 g. (20% excess) of sodium sulfite dissolved in 90 cc. of water and 50 cc. of alcohol. The mixture was refluxed for three and one-half hours, after which the alcohol was distilled off.

One cc. of 98% sulfuric acid was added and a rapid current of air was passed through the solution at 80° for ten minutes to expel sulfur dioxide and oxides of nitrogen. The cooled solution was extracted twice with ether and then neutralized with sodium carbonate and evaporated to dryness. The residue was extracted three times with 95% alcohol. The combined alcohol extracts were evaporated to 8 cc. and diluted with 35 cc. of ether. The sodium salt of the sulfonic acid separated and was filtered off and washed with ether; yield, 7.0 g. A second crop was isolated from the filtrate and washings; total yield, 8 g. or 70%.

Summary

1. Aryl sulfonic acid salts, when heated with phosphorus pentabromide, are converted to the corresponding aryl sulfonyl bromides and diaryl disulfides.

[17] Otto, *Ber.*, **15**, 131 (1882); **19**, 1239 (1886); **24**, 713 (1891).

[18] Blanksma, *Rec. trav. chim.*, **27**, 46 (1908).

[19] *Cf.* Willgerodt, *J. prakt. Chem.*, [2] **32**, 117 (1885).

2. The relative yields of sulfonyl bromide and di-aryl disulfide depend upon the nature of the aryl radical: in some cases the disulfide is the only product; in other cases it is formed in very small amounts.

3. In these reactions the sulfonyl bromide is formed first. It is subsequently reduced by the phosphorus tribromide, simultaneously formed by the dissociation of phosphorus pentabromide. The sulfonic acid salts are unaffected by phosphorus tribromide alone.

4. Aryl sulfonyl bromides are readily reduced by phosphorus tribromide; sulfonyl chlorides are reduced with much greater difficulty by the same reagent. Neither the sulfonyl chlorides nor bromides are reduced by phosphorus trichloride.

5. By the use of the bromides of phosphorus certain disulfides, otherwise difficult or impossible to prepare, are readily obtained.

6. One disulfoxide was investigated. It was reduced with extraordinary ease by phosphorus tribromide.

7. In some cases where the reaction products, containing excess phosphorus tribromide, were decomposed with water and ether, the sulfonyl compounds were reduced to the thiophenols.

8. Addition of bromine to an apparently incompletely reacted mixture in the course of an Otto synthesis of a sulfinate gave a new mixed disulfoxide.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE MACKAY CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA]

ESSENTIAL OIL IN DESERT PLANTS. II. EXAMINATION OF THE OIL OF CHRYSOTHAMNUS NAUSEOSUS

BY MAXWELL ADAMS AND LEWIS KEHOE

RECEIVED JANUARY 18, 1932 PUBLISHED JUNE 6, 1932

In a former article by one of us[1] attention has been called to the occurrence and physical properties of the essential oil of *Chrysothamnus Nauseosus*. Coulter and Nelson[2] list eighteen species and four additional varieties of *Chrysothamnus* growing in the arid plateau region of the United States. This entire group of shrubs is known to the western stock men as "Fall Rabbit Brush." Some attention was called to this plant by the work of Hall,[3] who found considerable quantities of rubber in the stems of this shrub. In our former work we collected small samples of oil from carefully selected plants of the following varieties of *Chrysothamnus: nauseosus*,

[1] Adams, THIS JOURNAL, **49**, 2895 (1927).

[2] Coulter and Nelson, "Manual of Botany of the Central Rocky Mountain Region," page 494.

[3] Harvey M. Hall and Thos. H. Goodspeed, University of California publications in Botany.

naphalodes, *viridulus*, *hololeucus* and *mohavensis*, but since these varieties grow together and can be distinguished only with difficulty, no attempt was made to segregate them in this mass collection. The raw material consisted chiefly of *nauseosus* yet small amounts of other species were present. There is very slight variation in the physical properties of the oils from these varieties, and the general chemical composition is doubtless very similar. The oil occurs chiefly in the leaves and small twigs. None was detected in the roots. The amount of oil present in a particular specimen of *Chrysothamnus* was determined by testing a sample gathered from the same plant each month during the year. The portion gathered in February contained the least, 0.39%, and this amount increased until it reached a maximum in October when there was 0.98% present. The amount of oil decreases when the autumn rains begin. A sample from plants grown on moist ground at Berkeley, California, contained only 0.2% of oil.

One sample of the oil was obtained as follows: 20 kg. of leaves and stems was distilled with steam for about twenty-four hours under pressure of about 2 lb. ($^1/_8$ atm.) until no more oil came over. The oil after separation was redistilled with steam and then dried over anhydrous sodium sulfate; 200 cc. of oil (sp. gr. 0.8651) was obtained corresponding to a material yield of 0.89%. Refraction tests of this oil showed only carbon, hydrogen and oxygen. The oil was insoluble in water and dilute acids, soluble to 2% in solutions of sodium acid sulfate, to 13% in dilute potassium hydroxide solution, and soluble in concentrated sulfuric acid to give a deep red color. It decomposes considerably when distilled at ordinary pressure, but gives a clear distillate at pressures below 100 mm.; 140 cc. of the oil distilled at 45 mm. gave fractions with the following properties.

Fraction	Range in temp., °C.	Yield, cc.	$d^{29°}$
1	90–100	60	1.4735
2	100–110	20	1.4781
3	110–167	30	1.4838
4	167–174	20	1.4970
5	174 (residue in flask)	10	1.5190

The lowest boiling fraction gave only the qualitative color test showing the presence of a small amount of α-pinene; 100 cc. of this fraction was oxidized with alkaline potassium permanganate according to the method of Wallach[4] and yielded nopinic acid which melted at 126°. When the alkaline permanganate residue was steam distilled, 40 cc. of oil was recovered, showing roughly that 60% of the oil had been oxidized. This indicates the presence of about 3% of β-pinene in the original oil.

The fraction boiling between 168 and 170° at 650 mm. was redistilled three times over metallic sodium until the boiling point was practically

[4] Wallach, *Ann.*, **245**, 251 (1888); *ibid.*, **356**, 229 (1907).

constant. The volume of the liquid thus obtained was composed of hydrocarbons. This fraction had a very strong odor of the oil of lemon and was tested for limonene. A bromine addition product was prepared which melted at 120°, indicating the presence of dipentene. The fraction however had a positive rotation of 59.4, which indicates the presence of limonene. Samples of *Chrysothamnus nauseosus* gathered at various places and at different seasons of the year showed great variation in the angle of rotation. Conditions under which the limonene tetrabromide will form do not appear to be well understood. Four fairly distinct methods have been recommended.[5] None of these methods gave uniformly dependable results. The following method gave us more satisfactory results than any of the above.

The oil to be tested is gently refluxed over metallic sodium for fifteen minutes and then distilled, preferably at reduced pressure, 10 to 20 mm. A second distillation over sodium is desirable. The fraction coming over between 172–178°, 760 mm. pressure, or a corresponding temperature at the reduced pressure, is then brominated as follows.

The fraction, or any part, is dissolved in an equal volume of ether. This terpene–ether solution is then added, drop by drop, to a well-cooled solution of bromine and ether. If all the bromine is not used up, more of the terpene–ether solution is prepared and added. If all the bromine is decolorized before all the terpene–ether solution is added, it is best to stop here and not attempt to add more bromine to the reaction mixture. The reaction mixture is placed at once in a desiccator, and by means of a suction pump the excess ether is boiled away. In the meantime the solution is kept cold. As the ether evaporates, the tetrabromide crystallizes out.

Fuchsine reagent shows an aldehyde present in the oil and it was separated by preparing the phenylhydrazone according to the usual method. After standing for several days clear white crystals, which may be washed free from the mother liquor with benzene, separated out. Recrystallized from alcohol the melting point was 126°. A small amount of the phenylhydrazone was hydrolyzed with concentrated hydrochloric acid, the product was evaporated to dryness, and the residue taken up with water. This water solution gave a strong aldehyde reaction with Tollens' reagent. From the amount, melting point, solubility and other properties of the phenylhydrazone it is concluded that the oil contains about 2% of cuminic aldehyde. About 20% of the oil of *Chrysothamnus nauseosus* has a boiling point of over 200° at ordinary pressure and 167° at 45 mm. pressure, which indicates the presence of sesquiterpenes. None were identified.

The results of the work outlined in this paper show that the essential oil of *Chrysothamnus nauseosus* contains about 3% β-pinene, 30 to 40% limo-

[5] Wallach, *Ann.*, **239**, 3 (1887); Baeyer and Villiger, *Ber.*, **271**, 448; Power and Kleber, *Arch. Pharm.*, **232**, 646 (1894); Godlewsky, *Chem.-Ztg.*, **22**, 827 (1898).

nene and dipentene, 2% cuminic aldehyde and 20% sesquiterpenes. That dipentene has been converted into caoutchouc[6] gives some interest to the fact that these two substances occur together in *Chrysothamnus* and suggests the question, may not the one be changed into the other by the plant metabolism?

[6] Gildemeister and Hoffman, I, p. 312.

RENO, NEVADA

[CONTRIBUTION FROM THE OKLAHOMA A. AND M. COLLEGE]

IDENTIFICATION OF NITRILES. PREPARATION OF ALKYL (2,4,6-TRIHYDROXYPHENYL) KETONES BY THE HOESCH SYNTHESIS ON A SEMI-MICRO SCALE

BY HENRY P. HOWELLS AND J. GLENN LITTLE[1]

RECEIVED JANUARY 18, 1932 PUBLISHED JUNE 6, 1932

In a recent attempt to find an easier means of identifying alkyl cyanides, Shriner and Turner[2] treated them with the Grignard reagent to give liquid ketones, which were converted finally to solid semicarbazones. Although the method has been found to be satisfactory when limited amount of starting material and time are not important factors, it was thought worth while to develop here a more rapid method in which very small amounts of nitriles could be used, as is recommended by Kamm, Mulliken[3] and others in qualitative organic analysis.

The present method adapts the Hoesch synthesis on a semi-micro scale, to give yields of products comparable to those described in the literature for similar preparations using much larger amounts of starting materials. Thus a small quantity of nitrile is combined with phloroglucinol to yield readily a solid phlorophenone in sufficient amount to make identification of the former very easy.

Experimental

A typical procedure for carrying out the modified Hoesch synthesis on a semi-micro scale is illustrated by the preparation of the new ketone in the series.

***n*-Butyl 2,4,6-Trihydroxyphenyl Ketone (Phloro-*n*-valerophenone)**, $C_6H_2(OH)_3$-COC_4H_9.—A solution of 0.006 mole of anhydrous phloroglucinol in about 25 cc. of dry ether was shaken up with 0.4 g. of pulverized, fused zinc chloride. To this was added 0.01 mole of *n*-butyl cyanide and a steady stream of dry hydrogen chloride gas about saturated with ether was passed through the mixture. After two to three minutes the

[1] The experimental routine of this paper was carried out largely by Mr. J. Glenn Little during an advanced course in organic preparations at Oklahoma A. and M. College.

[2] Shriner and Turner, THIS JOURNAL, **52**, 1267 (1930).

[3] O. Kamm, "Qualitative Organic Analysis," J. Wiley and Sons, 1923; Mulliken, "Identification of Pure Organic Compounds," J. Wiley and Sons, N. Y., 1905.

solution turned milky and in the course of a few more minutes became clear. At the end of fifteen minutes an amber colored oil[4] separated out. The reaction was allowed to continue for about ten minutes longer and then the supernatant liquid was decanted. The oil was taken up in 25 cc. of water and washed twice with 50 cc. of ether. The aqueous layer was concentrated to about one-half of its volume by heating. Upon cooling, long, silky needles separated which after two recrystallizations from hot water with norite gave colorless needles and when air-dried melted at 87–88° (corr.). The substance after drying in vacuum at 110° for thirty minutes or in a vacuum desiccator for a few hours lost a molecule of water to give the anhydrous ketone which melted at 149° (corr.); yield, 84.7%.

The crystals dissolved in concentrated sulfuric acid to give a deep yellow color and in dilute ferric chloride solution to form a purple-red color.

Anal. Calcd. for $C_{11}H_{14}O_4 \cdot H_2O$: H_2O, 7.9. Found: 8.2. Calcd. for $C_{11}H_{14}O_4$: C, 62.81; H, 6.72. Found: C, 62.96; H, 6.59.

The properties of the above ketone together with those of other members of the series are summarized for convenience in Table I. Each ketone gave a yellow color in concentrated sulfuric acid.

TABLE I

PROPERTIES OF KETONES OBTAINED BY THE ACTION OF 0.006 MOLE OF PHLOROGLUCINOL ON 0.01 MOLE OF NITRILE BY THE METHOD DESCRIBED

Only those nitriles studied by Shriner and Turner[1] are included here

Nitrile	Ketone	Yield, %	M. p., °C., corr. air-dried	M. p., °C., corr. vac.-dried	Crystal form	Color in $FeCl_3$ soln.
CH_3CN	$C_6H_2(OH)_3COCH_3$	93	218–218.5[a]	218.5[a]	Colorless needles	Cherry-red
C_2H_5CN	$C_6H_2(OH)_3COC_2H_5$	73.3	174–175.5[b]	175–176[b]	Colorless needles	Brownish-red
n-C_3H_7CN	$C_6H_2(OH)_3COC_3H_7$-*n*[c]	71.7	180–181[d]	181[d]	Colorless needles	Cherry-red
n-C_4H_9CN	$C_6H_2(OH)_3COC_4H_9$-*n*	84.7	87–88	149	Colorless needles	Purple-red
n-$C_5H_{11}CN$	$C_6H_2(OH)_3COC_5H_{11}$-*n*	68.5	95–96[e]	120–121[e]	Colorless needles	Purple-red
i-$C_5H_{11}CN$	$C_6H_2(OH)_3COC_5H_{11}$-*i*	37.2	103–104[f]	122.5[f]	Colorless needles and plates	Brown-red

[a] Bülow and Wagner, *Ber.*, **34,** 1798 (1901), report no melting up to 280° and give an analysis for $C_8H_8O_4$ (no hydrate); Heller, *Ber.*, **45,** 418 (1912) gives 209–210° and analysis for $C_8H_8O_4 \cdot H_2O$; Leuchs and Sperling, *ibid.*, **48,** 135 (1915), give sintering at 200° and melting at 218°, with analysis for $C_8H_8O_4$ and a monohydrate; Hoesch, *ibid.*, **48,** 1122 (1915), gives 218° and analysis for $C_8H_8O_4$ and a monohydrate; Sen and Ghosh, *J. Chem. Soc.*, **117,** 61 (1920), give 284–285° and analysis for $C_8H_8O_4$. Rosenmund and Schulz, *Arch. Pharm.*, **265,** 308 (1927), give 218° with sintering at 205°. Shriner and Kleiderer, THIS JOURNAL, **51,** 1267 (1929), give 213–214° (corr.) and analysis for $C_8H_8O_4$ making no mention of a hydrate although water was used as a recrystallizing solvent.

[b] Canter, Curd and Robertson, *J. Chem. Soc.*, 1245 (1931), report a monohydrate and m. p. 174–175°.

[c] Fabriken Vorm. Meister, Lucius and Bruning, British Patent 157,854 (1921), obtained the ketone from *n*-propyl cyanide, phloroglucinol, dry hydrogen chloride and ether, after hydrolyzing the ketimide hydrochloride by acidifying and boiling in water.

[d] Karrer, *Helv. Chim. Acta*, **2,** 466 (1919), and Karrer and Rosenfeld, *ibid.*, **4,** 707

[4] The oil, which must be a ketimide hydrochloride addition product, appeared in some of these syntheses as colorless crystals and in the preparation of phloro-*n*-caprophenone it did not appear. In the latter instance ice-cold water was added directly to the ether solution and the aqueous layer was worked up in the usual manner.

(1921), give 179–180° for the anhydrous form and an analysis of a monohydrate, for which no m. p. is recorded.

[e] Klarmann and Figdor, THIS JOURNAL, **48**, 803 (1926), give 95° for air-dried and 118° for vacuum dried at 100°. They give analysis for $C_{12}H_{10}O_4$ and do not state the degree of hydration.

[f] Karrer and Rosenfeld, *Helv. Chim. Acta*, **4**, 707 (1921), give 122° for the anhydrous form and 104° for the monohydrate.

Summary

A number of the more common alkyl cyanides have been combined with phloroglucinol in the Hoesch synthesis on a semi-micro scale to give good yields of phlorophenones which may be used conveniently as solid derivatives in the identification of the nitriles.

The ketones have been studied and their properties described.

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION AND PROPERTIES OF TERTIARY BUTYL PHENYLACETATE

BY DAVID L. YABROFF AND C. W. PORTER

RECEIVED JANUARY 21, 1932 PUBLISHED JUNE 6, 1932

In the course of our work on the nitration of phenylacetic acid and its esters it became necessary for us to synthesize tertiary butyl phenylacetate. This compound is not easily made by direct esterification of phenylacetic acid and hitherto its preparation has not been reported. By a modification of a method used by Houben[1] in the preparation of terpineol acetate we have succeeded in preparing pure tertiary butyl phenylacetate in yields equal to 65% of the theoretical. Since our procedure can be used to obtain other esters from tertiary alcohols and acids of high molecular weight, it seems worth while to describe the method.

A halomagnesium alcoholate is prepared by decomposing ethylmagnesium bromide with tertiary butyl alcohol

$$C_2H_5MgBr + (CH_3)_3COH \longrightarrow MgBrOC(CH_3)_3 + C_2H_6$$

The alcoholate, a white solid, is kept suspended and finely divided by vigorous mechanical stirring. An ether solution of phenylacetyl chloride is added to the ether suspension of the halomagnesium alcoholate and the reaction mixture is warmed under a reflux condenser.

$$C_6H_5CH_2COCl + MgBrOC(CH_3)_3 \longrightarrow C_6H_5CH_2COOC(CH_3)_3 + MgBrCl$$

A greater yield of the ester is obtained when the mixture is refluxed for one hour than when it is refluxed for a longer time. This is probably due to a gradual conversion of the ester into phenylacetic acid. In the longer runs we actually isolated phenylacetic acid in quantities sufficient to account for the failure to obtain a one hundred per cent. yield of the ester.

[1] Houben, *Ber.*, **39**, 1763 (1906).

Experimental

Bromomagnesium tertiary butylate was prepared in solid form by adding a slight excess of tertiary butyl alcohol to ethylmagnesium bromide and warming the mixture to drive off ethane. Most of the ether was decanted from the solid alcoholate and the rest was removed by passing dry air over the surface of the residue. The alcoholate was then dried under reduced pressure over calcium chloride. It was found to retain one molecule of ether of crystallization. The equivalent weight as determined by titration with standard silver nitrate solution (K_2CrO_4 indicator) was 234–235; calcd. for $MgBrOC_4H_9 \cdot C_2H_5OC_2H_5$, 239.

Preparation of the Ester

Through the Grignard Reaction.—The solid halomagnesium alcoholate was allowed to react with phenylacetyl chloride with one and then the other in excess in different experiments. The time of refluxing also was varied. It made no difference in yield whether the alcoholate or the phenylacetyl chloride was in excess, but the presence of unchanged phenylacetyl chloride made the separation and purification of the ester difficult. From these preliminary experiments the following final procedure was developed.

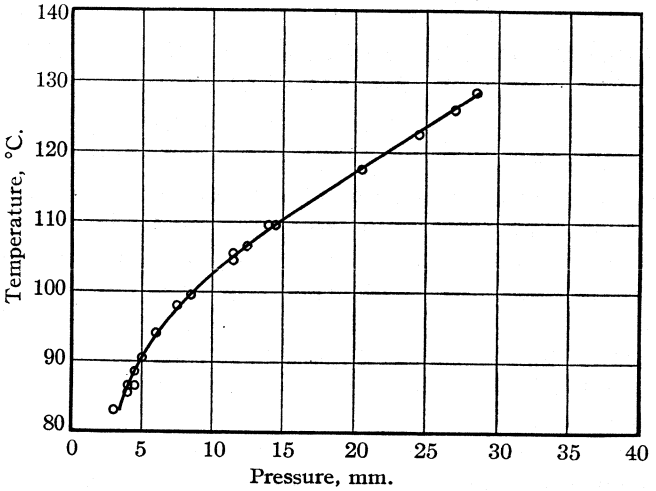


Fig. 1.—Boiling point curve for tertiary butyl phenylacetate.

A solution of 40 g. of tertiary butyl alcohol (0.54 mole) in 50 cc. of ether was added very slowly to approximately one-half mole of ethylmagnesium bromide in 300 cc. of anhydrous ether. The $MgBrOC_4H_9$ which formed as an insoluble white substance was kept in suspension by stirring. The mixture was then warmed to the boiling point of the ether and refluxed for fifteen minutes. Then 46.1 g. of phenylacetyl chloride (0.3 mole) in 50 cc. of ether was added slowly to the hot reaction mixture and refluxing was resumed for one hour.

The content of the flask was then poured on to ice and acidified with dilute sulfuric acid. The ether layer was separated, washed successively with ice-cold water, cold dilute sodium hydroxide solution, and again with cold water. A clear orange-brown liquid remained after the ether had been distilled off. This was fractionated under reduced pressure. Figure 1 shows the boiling points of the ester at various pressures.

By a Direct Method.—Phenylacetic acid was dissolved in a large excess of tertiary butyl alcohol in the presence of a small amount of concentrated sulfuric acid and the

mixture was allowed to stand at room temperature for twenty days in one case and for sixty days in another case. The yields of ester obtained in this way were very small.

Refractive Index of the Ester.—Samples of approximately 25 g. of the ester from each of five preparations were separately purified by fractional distillation. Three of the preparations were made through the Grignard reaction and two were obtained by the direct esterification of the acid by the alcohol. After each fractionation the refractive index of the middle portion of each preparation was determined at 25°. Although the measurements made on different samples were not in agreement, the refractive index of each sample remained nearly constant through repeated distillations. Each preparation was then purified by dissolving the ester in ether and washing with dilute sodium hydroxide solution, dilute sulfuric acid solution, and finally with water. The ether was dried over calcium chloride, distilled off and the ester was fractionated again under reduced pressure. This treatment produced no appreciable change in the refractive index. The last trace of impurity cannot be removed from this ester by repeated washings, extractions and distillations. The refractive index may remain constant on successive distillations and still be incorrect. A similar case is seen in the values reported for tertiary butyl acetate by Henry[2] and by Smith and Olsson.[3]

Purification was finally accomplished by fractional crystallization of the compound. A sample of the ester (50 g.) was dissolved in freshly distilled pentane and the mixture was cooled with liquid air. The ester separated as a white snow-like solid. Most of the pentane (which contained about 10 g. of dissolved ester) was decanted, more pentane was added, and the process was repeated a second time. The ester obtained in the second crystallization from pentane was pure and its index of refraction was 1.4825. The density of tertiary butyl phenylacetate (d_4^{25}) was found to be 0.9758 ±0.0004, whence the molecular refraction (M_D) by the Lorentz–Lorenz equation becomes 56.19.

Melting Point of the Crystalline Ester.—When the ester is cooled with a mixture of solid carbon dioxide and ether it becomes viscous but fails to crystallize until inoculated with some of the solid ester obtained by cooling a pentane solution of the ester with liquid air. The crystals melt at −23 to −21°. The melting range was obtained in the usual manner by means of warming curves.

Summary

A method is described for the preparation of tertiary butyl phenylacetate which gives a yield of the purified ester equal to about 65% of the theoretical quantity. Physical properties, including boiling points at various pressures, the melting range and the refractive index of the compound have been reported. It is shown that a preparation of this ester which boils at the same temperature after repeated distillations may show a constant but erroneous refractive index.

BERKELEY, CALIFORNIA

[2] Henry, *Rec. trav. chim.*, **26**, 438 (1907).

[3] Smith and Olsson, *Z. physik. Chem.*, **118**, 99 (1925).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. VI. THE SYNTHESIS OF 4-HYDROXY-3,5-DIBROMO-2′,6′-DIIODO-4′-CHLORODIPHENYL ETHER AND THE DECOMPOSITION OF ITS METALLIC SALTS[1]

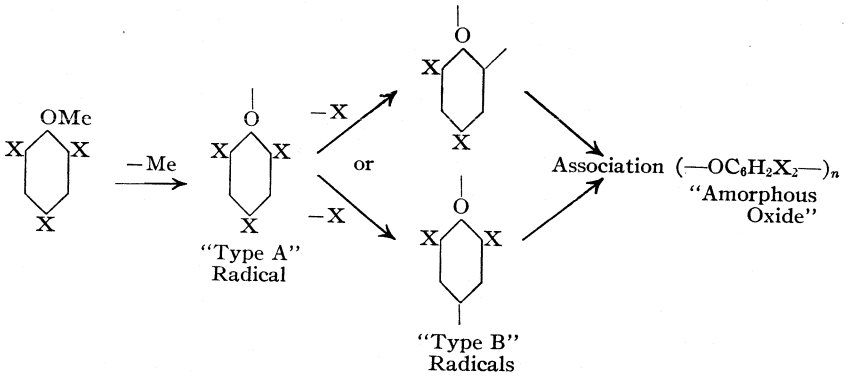
BY W. H. HUNTER AND MILES A. DAHLEN[2]

RECEIVED JANUARY 28, 1932 PUBLISHED JUNE 6, 1932

Introduction

Earlier investigations in this Laboratory and elsewhere by Hunter and his students[3] have been concerned with the decomposition of the metallic salts of the symmetrically trihalogenated phenols and related compounds. These decompositions have been observed to take place under the influence of certain catalysts, such as the halogens and alkyl halides, and also may be induced by heating the dry salts of the trihalogenated phenols, suspended in an inert medium such as benzene.

As a result of these studies, it has been suggested that the decomposition of these metallic salts under the influence of heat or catalysts proceeds through the following steps



It has been shown that the amorphous oxides are formed by the union of Type B radicals, involving the formation of new oxygen-to-carbon bonds, *i. e.*, that the association results in linkages of the diphenyl ether type. No evidence has been found for the formation of new carbon-to-

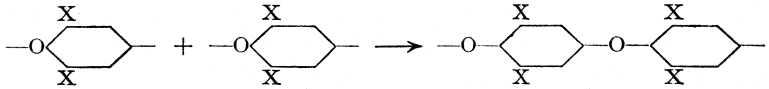
[1] This paper was prepared from a portion of the Thesis of M. A. Dahlen presented to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1928. The manuscript was written by the junior author after the death of Dr. Hunter in 1931.—L. I. SMITH.

[2] Du Pont Fellow in Chemistry, University of Minnesota, 1927–1928.

[3] (a) Torrey and Hunter, THIS JOURNAL, **33**, 204 (1911); (b) Hunter and others, *ibid.*, **38**, 1761, 2474 (1916); (c) **39**, 2640 (1917); (d) **43**, 131, 135, 151 (1921); (e) Lauer, Thesis, University of Minnesota, 1924; (f) Whitney, THIS JOURNAL, **54**, 1167 (1932); (g) Rathmann, Thesis, University of Minnesota, 1927.

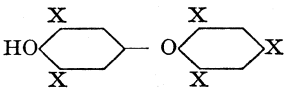
carbon and oxygen-to-oxygen bonds; indeed, tests for peroxides, which would result from the latter type of union, have given negative results in every case.

Therefore, the first stage of this association process may be expressed as follows, assuming that it involves the union of two Type B radicals resulting from the loss of halogen from the para positions of the corresponding Type A radicals

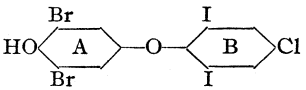


Since the union of radicals of Type A and Type B leads to the formation of products containing linkages of the diphenyl ether type, it was hoped that the preparation and study of a halogenated phenol related to the symmetrically trihalogenated phenols, but already containing a diphenyl ether linkage similar to that present in the oxidation products and amorphous oxides, would cast further light on the nature of the decomposition and oxidation processes previously studied.

A halogenated phenol of the structure (A) was selected as most closely related to the amorphous oxides and trihalophenoxyquinones obtained in the previous work. In order that the subsequent experiments on the



A



I

decomposition of the metallic salts of the phenol should provide a maximum of information concerning the lability and reactivity of the various halogen atoms, the product actually synthesized was (I). By "labeling" the various non-equivalent positions in the molecule with different halogens, the interpretation of the results of subsequent decomposition experiments was rendered extremely easy.

Decomposition of the Metallic Salts of the New Phenol.—A preliminary consideration of the possibilities involved in the decomposition of the metallic salts of the new phenol suggested that one of the following results might be expected.

(1) The salts might not decompose under the conditions which cause amorphous oxide formation from the salts of the trihalogenated phenols.

(2) The salts might decompose in a manner analogous with the decomposition of salts of the trihalogenated phenols, and the loss of halogen from the Type A radical first obtained would be confined to Ring "A." The products of such a decomposition would be an amorphous oxide and the metal bromide.

(3) A decomposition would result in which the loss of halogen from the Type A radical would be confined to Ring "B." The products of such

a decomposition would be an amorphous oxide and the metal iodide, chloride, or a mixture of the iodide and chloride.

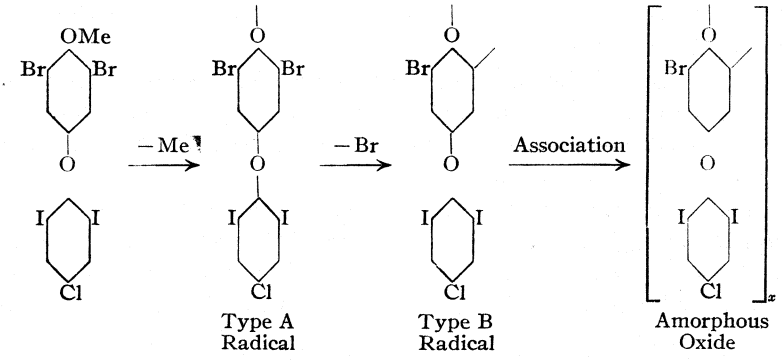
(4) A decomposition would result which would involve all the halogens present in the molecule. The products of such a decomposition would be an amorphous oxide and the mixture of the metal chloride, bromide and iodide.

The potassium salt of the new phenol was decomposed in water solution by the addition of a trace of bromine, following the procedure used in the earlier work on the metal salts of the trihalogenated phenols. The colorless solution of the phenol salt momentarily turned blue-green, then became colorless and a copious precipitate of the white amorphous oxide appeared. The behavior was entirely analogous to the action of the potassium salt of a trihalogenated phenol under the same conditions.

The solution was tested qualitatively for the halogens, but the bromide ion alone was present. The amorphous oxide was analyzed for total halogen and also for the various halogens, and the results were found to correspond closely with the empirical formula $(C_{12}H_4O_2ClBrI_2)_x$. These results indicated that the decomposition had proceeded according to "2" above.

The silver salt of the new phenol was decomposed in benzene suspension by the action of ethyl iodide, iodine and heat, respectively. In each case an amorphous oxide was obtained corresponding with the above empirical formula. The silver halide produced by the decomposition under the influence of heat alone was examined carefully and found to be silver bromide. No trace of iodide or chloride could be found.

The above experiments demonstrated that the decompositions of the salts of the new phenol had taken place in the following manner, assuming that the mechanism previously proposed may be applied to these analogous decompositions

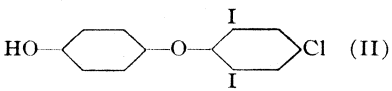


Discussion of the Results

The fact that metallic salts of the new halogenated phenol decomposed in a manner analogous to the decomposition of salts of the symmetri-

cally trihalogenated phenols was not especially surprising, even though the decomposition reaction was confined to the benzene nucleus containing only two halogen atoms; for recent work by Rathmann in this Laboratory[3g] has disclosed that the salts of dihalogenated ortho and para cresols may be decomposed in a similar manner. However, the fact that halogen atoms were removed only from the hydroxyl-bearing nucleus seems to be most important, especially since in the molecule studied the other benzene nucleus was substituted by three halogen atoms oriented as in the trihalogenated phenols previously studied. On the basis of previous work, it might be expected that the halogen atoms in Ring "B" would be as reactive or labile as those in Ring "A." The fact that all halogen loss occurs from Ring A must be interpreted as meaning that the influences responsible for decompositions of this type are confined to the ring bearing a free hydroxyl group. The conversion of a trihalogenated phenol to an ether apparently results in diminution or complete disappearance of these influences.

In order to check this point, an attempt was made to decompose the salts of the phenol II, which was prepared as an intermediate in the synthesis of I. It was found that the salts of II did not decompose under the conditions which result in rapid amorphous oxide formation in the case of I and of the ordinary trihalogenated phenols. Similar experiments on the salts of 4-hydroxy-2′,6′-diiodo-4′-bromodiphenyl ether also gave negative results. These experiments seemed to prove that the hydroxyl group must be present in the halogenated nucleus in order that this type of decomposition may occur.



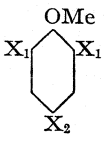
(II)

A second important result of this study was the disclosure of additional evidence for the existence of radicals of Type A and Type B. First of all, the momentary appearance of a blue-green color, followed by decoloration and precipitation of the amorphous oxide during the decomposition of the phenol salts, coincides with the behavior of the ordinary trihalogenated phenol derivatives. The colored intermediate products have been assumed, in previous work, to be the free radicals. The present work adds strength to the previous theory, since similar observations have now been made on substances quite different in chemical constitution.

More important, however, is the fact that the results of the present study make it appear less likely than ever that the metallic salt decompositions are intermolecular reactions involving the "splitting-off" of metal halide between molecules, forming the diphenyl ether type linkages. If such a mechanism actually were correct, then it would appear most probable that halogen atoms in Ring B of I would be involved. A correlation of the work of Hunter and Joyce[4] on the decomposition of salts of

[4] Hunter and Joyce, THIS JOURNAL, **39**, 2640 (1917).

the type indicated, where X_1 and X_2 are different halogens, with the results of the new decompositions, would indicate that a reaction mechanism involving intermolecular reaction is almost mathematically impossible in the case of certain trihalogenated phenols of the above type. This is especially true in the case where X_1 represents Cl and X_2 is Br. If intermolecular condensation is not possible as an explanation of the decompositions, the mechanism involving the Type A and Type B radicals receives added confirmation.



Experimental Part

4-Methoxy-2′,6′-diiodo-4′-nitrodiphenyl Ether.—The above substance was prepared according to the synthesis described by Harington and Barger.[5]

This method was found to give excellent results when pure starting materials were used. However, the reaction failed entirely when impure ethyl methyl ketone was used as a solvent, and gave poor results unless the other starting materials were of high purity. The best experiments in this work gave condensation yields of 70% of the theoretical, as compared with the 67% yield reported by the above authors.

4-Methoxy-2′,6′-diiodo-4′-aminodiphenyl Ether Hydrochloride.—The method of Harington and Barger was used for the reduction of the above nitro compound to this amine. The yield was usually about 65% of the theoretical.

4-Methoxy-2′,6′-diiodo-4′-chlorodiphenyl Ether.—Twenty-five grams of the hydrochloride of 4-methoxy-2′,6′-diiodo-4′-aminodiphenyl ether was ground very finely in an agate mortar. It was then suspended in 150 cc. of glacial acetic acid to which had been added 10 cc. of water. The suspension was agitated with a high-speed stirrer and cooled externally to 15°. Eight cubic centimeters of *tert.*-amyl nitrite was now added slowly, the temperature being held at 15°. The mixture was then stirred at this temperature for one-half hour, to allow the diazotization to go to completion.[6]

Fifty grams of cuprous chloride was dissolved in 250 cc. of concd. hydrochloric acid and 150 cc. of water was added to the solution. It was then heated to about 60° on the steam-bath, and the diazo solution prepared as above added slowly with vigorous stirring. Much nitrogen was evolved, and the product settled out as a black oil. The mass was heated on the steam-bath for about one hour to complete the replacement, and was then cooled to room temperature. The product solidified to a black crystalline mass and was filtered. It was dissolved in benzene, dried overnight over calcium chloride, and the benzene removed by distillation at atmospheric pressure. The product was then distilled in a vacuum. The fraction boiling at 200–218° under 4 mm. pressure was collected. It distilled as a yellow oil which quickly solidified. The yield at this point was 15.4 g. or about 64% of the theoretical. The product was recrystallized from a mixture of 67 parts absolute alcohol and 33 parts benzene until it showed a constant melting point.

Anal. (Carius) Calcd. for $C_{13}H_9O_2ClI_2$: Cl, 2I, 59.47. Found: X, 59.41, 59.21.

The product crystallizes from alcohol in long white plates melting at 101–102°.

---

[5] Harington and Barger, *Biochem. J.*, **21**, 175 (1927).

[6] Harington and Barger used the above method of diazotization in the conversion of this base to the corresponding nitrile. It was found in the present work that the use of *tert.*-amyl nitrite gave better results than the mixture of amyl nitrites prepared from commercial amyl alcohol. It was also found that the addition of a small quantity of water facilitated the diazotization process.

4-Methoxy-2',6'-diiodo-4'-bromodiphenyl ether.—This material was prepared by a process similar to the above. The product crystallizes from alcohol in bunches of white plates, melting at 123–123.5°, and boiling at 209–219° under 2 mm. pressure.

Anal. (Carius). Calcd. for $C_{13}H_9O_2BrI_2$: Br, 2I, 62.87. Found: X, 62.78, 62.62.

4-Methoxy-2',4',6'-triiododiphenyl Ether.—This material, similarly prepared, showed the following properties.

Anal. (Carius). Calcd. for $C_{13}H_9O_2I_3$: I, 65.89. Found: I, 65.92, 65.72.

The substance crystallizes from a benzene–alcohol mixture in white needles melting at 132–132.5°, and boiling at 220–230° under 1–2 mm. pressure.

4-Hydroxy-2',6'-diiodo-4'-chlorodiphenyl Ether.—Five grams of the corresponding methoxy compound was dissolved in 35 cc. of boiling glacial acetic acid, 0.1 g. of red phosphorus added, and then 44 cc. of pure 57% hydriodic acid was poured in through the reflux condenser. The mixture was held at the boiling point until all of the methoxy compound, which separated as an oil upon the addition of hydriodic acid, redissolved. The mixture was then cooled and poured into an equal volume of water, precipitating the phenol as a white solid.

The crude product obtained as above was dissolved in warm dilute sodium hydroxide solution, filtered, and the phenol reprecipitated by the addition of hydrochloric acid. The product was filtered, washed with water, and then crystallized from 50% alcohol. The yield at this point was about 82% of the theoretical. Repeated crystallization from alcohol gave a product melting sharply at 154.5°. The hydroxy compound crystallizes in the form of very small white needles. The sodium and potassium salts of the phenol are only slightly soluble in cold water, but dissolve readily at the boiling point.

Anal. (Carius). Calcd. for $C_{12}H_7O_2ClI_2$: Cl, 2I, 61.24. Found: X, 60.57, 60.55.

4-Hydroxy-2',6'-diiodo-4'-bromo-diphenyl Ether.—This phenol was prepared from the corresponding methoxy compound by a process similar to the above. It crystallizes from alcohol in white needles melting at 162–163°. The sodium and potassium salts are quite insoluble in cold water but dissolve readily at the boiling point.

Anal. (Carius). Calcd. for $C_{12}H_7O_2BrI_2$: Br, 2I, 64.57. Found: X, 64.54, 64.47.

4-Hydroxy-3,5-dibromo-2',6'-diiodo-4'-chlorodiphenyl Ether.—2.7 grams of 4-hydroxy-2',6'-diiodo-4'-chlorodiphenyl ether was dissolved in 20 cc. of glacial acetic acid in an acetylating flask, and the solution was heated to about 75°; 1.88 g. (3% excess) of bromine was dissolved in 20 cc. of glacial acetic acid and added to the solution of the phenol through the reflux condenser. The solution was heated to boiling for ten minutes, cooled and poured into about 200 cc. of water. The phenol was filtered, washed with water, and crystallized from a mixture of chloroform and alcohol. It was then crystallized repeatedly from absolute alcohol containing a little benzene until a product melting at 194.5° was obtained. The yield on bromination was practically the theoretical, but much material was lost in the purification process.

Anal. (Carius). Calcd. for $C_{12}H_5O_2ClBr_2I_2$: Cl, 2Br, 2I, 71.26. Found: X, 70.92.

The phenol crystallizes from absolute alcohol in white micro needles. It is very slightly soluble in alcohol, moderately soluble in benzene and very soluble in chloroform. The sodium and potassium salts are quite insoluble in cold water but dissolve readily on heating.

Silver Salt of 4-Hydroxy-3,5-dibromo-2',6'-diiodo-4'-chlorodiphenyl Ether.—One gram of the phenol was dissolved in 30 cc. of hot, very dilute sodium hydroxide. The solution was filtered and cooled, the sodium salt separating from the filtrate in white plates. The sodium salt was filtered, washed with a little cold water, and then suspended in 20 cc. of distilled water. The suspension was heated to bring the salt into solution,

then cooled rapidly in order to obtain the product in the form of very fine crystals. Two-tenths gram of pure silver nitrate was dissolved in distilled water and added to the suspension of the sodium salt. The silver salt immediately formed as a gelatinous white solid. It was filtered, washed with water and dried overnight in a vacuum desiccator.

Catalytic Decomposition of the Potassium Salt of 4-Hydroxy-3,5-dibromo-2',6'-diiodo-4'-chlorodiphenyl Ether. A. By Bromine.—Three grams of the phenol was dissolved by heating with 25 cc. of a very dilute solution of potassium hydroxide. A cubic centimeter of bromine water was then added. The solution immediately turned bluish-green, and an amorphous oxide quickly appeared as an almost white gelatinous precipitate. The solution was boiled for one-half hour to insure complete decomposition. It was then filtered, and the oxide was collected and dried. The filtrate was reserved for qualitative tests for halogen (see below).

The oxide was purified by dissolving in 20 cc. of warm benzene, filtering, and reprecipitating by the addition of 40 cc. of low-boiling ligroin. The process was repeated four times and the product was then white and practically pure; melting point, 245–257° with decomposition. The yield of crude amorphous oxide was 2.2 g., corresponding to 85% of the theoretical. About 2 g. of purified material was obtained from this crude product.

Anal. (Carius) Calcd. for $(C_{12}H_4O_2ClBrI_2)_x$: Cl, Br, 2I, 67.21. Found: X, 66.38, 66.17. *Analysis* of silver salts by electrolysis: 0.2967 g. of mixed silver salts gave 0.1592 g. Ag. Calcd. for AgCl, AgBr, 2AgI: 0.1599.

Tests for Halogen in Filtrate from Amorphous Oxide Precipitation.—The filtrate from the above decomposition of the potassium salt was acidified with nitric acid and filtered. A little pure sodium bisulfite was added to reduce all halogen to halide ion, and the solution boiled to remove excess bisulfite. It was then extracted with benzene to remove organic matter.

The solution was now tested for each of the halide ions by the usual qualitative procedure. The test for bromide ion was positive; all other halides were absent.

B. By Iodine.—Another sample of the phenol was treated in the same manner, except that a drop of a solution of iodine in potassium iodide was substituted for bromine water. Apparently the same decomposition took place and the same amorphous oxide was produced. Analyses of the amorphous oxide corresponded with the results given above. The filtrate from this decomposition was also tested for halide ions, and was found to contain bromide and iodide ions. The iodide ion undoubtedly was introduced by the decomposition catalyst.

Catalytic Decomposition of the Silver Salt of 4-Hydroxy-3,5-dibromo-2',6'-diiodo-4'-chlorodiphenyl Ether. A. By Ethyl Iodide.—A small sample of the dry salt was suspended in 5 cc. of dry benzene. A drop of ethyl iodide was added. The solution turned bluish-green in color almost immediately. This color persisted for about ten minutes, then disappeared, and the solution remained a light yellow. The solid remaining was filtered and qualitative tests showed it to be silver bromide mixed with a little unchanged silver salt. The addition of an equal volume of ligroin to the filtrate precipitated an amorphous oxide. Analysis of this material showed it to be identical with the product obtained from the decomposition of the potassium salt.

B. By Iodine.—The above experiment was repeated, using a small crystal of iodine instead of ethyl iodide as the catalyst. The same decomposition occurred, yielding the same products.

C. By Heat.—A small sample of the silver salt was suspended in 5 cc. of benzene and the solution heated to about 70°. The mass turned blue-green momentarily, then faded to a pale yellow. A precipitate of silver bromide was obtained, and from the filtrate the same amorphous oxide was isolated.

Attempted Catalytic Decomposition of the Potassium and Silver Salts of 4-Hydroxy-2′,6′-diiodo-4′-chlorodiphenyl Ether.—The potassium and silver salts of 4-hydroxy-2′,6′-diiodo-4′-chlorodiphenyl ether were prepared by the usual methods. They were subjected to the action of the above catalysts under similar conditions, but in no case did a decomposition to amorphous oxide occur.

Summary

1. 4-Hydroxy-3,5-dibromo-2′,6′-diiodo-4′-chlorodiphenyl ether, a new halogenated phenol related to the symmetrically trihalogenated phenols, has been prepared.

2. The catalytic decomposition of metallic salts of the new phenol has been studied. The decomposition occurs in a manner entirely analogous to that of the trihalogenated phenols previously studied. It was observed that only the halogen in the hydroxyl-bearing nucleus is removed in such decomposition.

3. Additional confirmation of the mechanism previously suggested for the catalytic decomposition of metal salts of halogenated phenols has been obtained.

4. Additional evidence for the existence of Type A and Type B radicals has been disclosed.

MINNEAPOLIS, MINNESOTA
WILMINGTON, DELAWARE

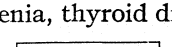
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. L.[1] THE SYNTHESIS OF HYDANTOINS POSSESSING THE PROPERTIES OF HYPNOTICS

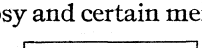
BY ROBERT M. HERBST[2] AND TREAT B. JOHNSON

RECEIVED JANUARY 29, 1932 PUBLISHED JUNE 6, 1932

That the hydantoin nucleus exhibits hypnotic properties has been known for several years. This pharmacological behavior is most pronounced in the drug "*nirvanol*" (phenylethylhydantoin) I, which is the hydantoin analog of the pyrimidine "*luminal*" or phenylethylbarbituric acid II. The latter cyclic ureide and several of its representatives have been used effectively as sedatives and hypnotics in simple insomnia, hysteria, neurasthenia, thyroid disease, chorea, epilepsy and certain mental disturbances.



I



II

Although nirvanol I has fallen into disrepute in recent years as an hypnotic because of the fever and skin eruptions induced by its continued ad-

[1] Constructed from a dissertation presented by Robert M. Herbst to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1930.

[2] Eli Lilly Company Graduate Scholar, 1928–1929.

ministration, it has recently been found to exert a valuable therapeutic action on certain nervous disorders. Several physicians working in hospitals have reported to this Laboratory remarkable successes in the clinical treatment of chorea (St. Vitus' dance) with this hydantoin I.[3] However, here too the drug must be administered continuously over a period of time, and the undesirable reactions are also manifested. Peculiarly, the disappearance of the characteristic skin eruptions and fever induced by nirvanol is coincident with the disappearance of the symptoms of chorea. The work discussed in this paper represents a part of a co-operative research program, organized for the purpose of synthesizing a group of new hydantoin derivatives which might be better suited than *nirvanol* to the treatment of chorea and other nervous disorders. Very little attention has thus far been paid to the pharmacology of this class of organic compounds.

For the preparation of dialkyl-hydantoins we have employed a method first applied by Urech[4] and recently studied by Read[5] of this Laboratory, and also by Biltz and Slotta,[6] whereby the desired hydantoins may be prepared from ketones in three steps as is expressed by the formulas

$$RCOR' + NH_4CN \longrightarrow RR'C(NH_2)CN \longrightarrow$$

$$RR'C(NHCONH_2)CN \longrightarrow HN{=}\overline{CNHCONHC}RR' \longrightarrow CONHCONHCRR'$$

IV V VI

In the third step of this process (IV ⟶ VI) we postulate that the reaction takes place through the formation of an intermediate imino-hydantoin V, which in strongly acid solution is immediately decomposed, giving the corresponding dialkyl-hydantoin VI. The conversion of the hydantoin nitrile IV to the hydantoin VI in hot acid solution proceeds with such rapidity that the reaction is practically instantaneous. This suggests that another reaction mechanism than that involved in the normal hydrolysis of a cyanide group, which is usually a slower reaction, is to be considered. In a previous paper[7] the authors have described a rearrangement of an hydantoic-nitrile IV, to a stable 4-aminohydantoin, a molecular change which, we believe, lends support to the mechanism of reaction suggested above.

[3] Private communication from Dr. S. W. Clausen of the Strong Memorial Hospital, University of Rochester, Rochester, New York. Also the drug has been used with success in the clinics of several medical schools, including Yale, during the past two years. See also "Phenylethylhydantoin in the Treatment of Syndenham's Chorea" by Ray and Cunningham, *Am. J. Diseases of Children*, **39**, 1205 (1930).

[4] Urech, *Ann.*, **164**, 255 (1872).

[5] See Read, THIS JOURNAL, **44**, 1746 (1922), for a review of the literature on methods of synthesis.

[6] Biltz and Slotta, *J. prakt. Chem.*, **113**, 233 (1926).

[7] Herbst and Johnson, THIS JOURNAL, **52**, 3676 (1930).

Experimental Part

Preparation of Ketones.—Several of the ketones employed in the synthesis of alkylated hydantoins were prepared by the catalytic method of Senderens,[8] in which thorium oxide carried on pumice served as the catalyst. Methyl benzyl ketone was prepared by passing the vapors of a mixture of acetic acid and phenylacetic acid over the catalyst at a temperature of 430–450°. Similarly ethyl benzyl ketone and ethyl β-phenylethyl ketone were prepared catalytically by heating mixtures of propionic acid with phenylacetic and hydrocinnamic acids, respectively. Varying amounts of the two possible symmetrical ketones are always formed as by-products and may be recovered. Benzylacetone was prepared for our research by reducing benzalacetone[9] with hydrogen gas at a pressure of 2 to 3 atmospheres in the presence of Adams' platinum oxide catalyst.[10]

The Preparation of Nitriles of Amino Acids from Ketones.—The amino acid nitriles corresponding to the ketones were prepared by the action of anhydrous hydrocyanic acid and ammonia on a solution of the respective ketone in absolute ethyl alcohol. These compounds are usually isolated most conveniently in the form of their hydrochlorides. The technique employed was as follows.

A solution of 0.25 mole of the ketone in 25 cc. of absolute ethyl alcohol is thoroughly cooled with ice water; 0.25 mole of anhydrous hydrocyanic acid is added, followed by 0.25 mole of anhydrous ammonia. During the addition of the ammonia the flask in which the reaction is applied is thoroughly cooled, and equipped with a good reflux condenser to prevent loss of hydrocyanic acid, since considerable heat is evolved in the formation of ammonium cyanide. This procedure is much more convenient than that previously recommended by Read[5] in which solid ammonium cyanide is first prepared for the reaction with the ketone.

The solution containing the ketone and ammonium cyanide is transferred to a pressure bottle, and the mixture allowed to stand from twenty-four to seventy-two hours until the reaction is complete, or equilibrium is established. The contents are then poured into a mixture of 200 g. of cracked ice and 50 cc. of concentrated hydrochloric acid. Any unreacted ketone separates as an oil, and may be removed by extraction with ether. The desired amino-nitrile is liberated by the addition of a slight excess of concentrated ammonia, keeping the solution well cooled by the addition of cracked ice. It separates as an oil which takes up in the ether and is separated from the aqueous layer, which is further extracted twice with fresh ether. The ether solutions are combined and dried over sodium sulfate. The hydrochloride of the amino-nitrile is precipitated from the ether solution by the addition of dry hydrogen chloride.

The hydrochloride of α-amino-α-methyl-γ-phenylbutyronitrile, from benzylacetone, precipitates practically completely from the acid water solution and the steps involving liberation of the aminonitrile and subsequent precipitation from ether solution are omitted in this case. The hydrochloride of 1-amino-1-cyanocyclohexane precipitates partially from the acid water solution. The remainder is obtained in the manner described above. The hydrochloride of α-amino-α-ethyl-γ-phenylbutyronitrile is not precipitated readily as a solid from ether solution with dry hydrogen chloride; consequently it was used as the free base, which was obtained by evaporating the ether from the dry solution of the amino-nitrile under reduced pressure at room temperature. A small amount of the hydrochloride was prepared by dissolving the amino-nitrile in dilute aqueous hydrochloric acid, and saturating the cold solution with hydrogen chloride,

[8] Senderens, *Ann. chim. phys.*, [8] **28,** 318 (1913).

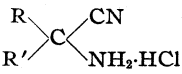
[9] Vavon, *Compt. rend.*, **154,** 1706 (1912).

[10] Adams and Shriner, THIS JOURNAL, **45,** 2171 (1923)

whereupon the hydrochloride of α-amino-α-ethyl-γ-phenylbutyronitrile precipitated in the form of colorless needles.

The new amino acid nitriles prepared in this research are recorded in Table I.

TABLE I



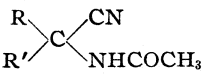
R	R′	Formula	M. p., °C. (corr.)	Calculated, % N	Cl	Found, % N	Cl	Yield,[a] %
CH_3	$CH_2C_6H_5$	$C_{10}H_{13}N_2Cl$	148–150	14.25	...	14.17 14.21	...	86.5
C_2H_5	$CH_2C_6H_5$[11]	$C_{11}H_{15}N_2Cl$	135–140	13.30	16.84	13.30 13.23	17.05	81
CH_3	$CH_2CH_2C_6H_5$	$C_{11}H_{15}N_2Cl$	140–141	13.30	...	13.28	...	88
C_2H_5	$CH_2CH_2C_6H_5$	$C_{12}H_{17}N_2Cl$	84	11.45	...	11.73	...	85
$CH_2(CH_2—CH_2)_2C$[12]		$C_7H_{13}N_2Cl$	202–204	17.45	22.08	17.42 17.20	22.35	77

[a] The yields are calculated allowing for recovered ketone, which never amounted to more than 25–30% of the original material.

The amino acid nitrile hydrochlorides are all soluble in water, somewhat soluble in 95% ethyl alcohol, and insoluble in most other organic solvents. The hydrochlorides of α-amino-α-methyl-γ-phenylbutyronitrile and 1-amino-1-cyanocyclohexane are stable; the rest decompose slowly on standing. Also the free nitriles are oils in the crude state, very slightly soluble in water, and somewhat unstable, especially toward heat. Since it was impossible to distil them under reduced pressure, purification was not attempted.

The acetylamino-nitriles were prepared by treating the free amino acid nitriles with acetic anhydride in the usual manner. The new compounds prepared are given in Table II.

TABLE II



R	R′	Formula	M. p., °C.	N Analyses, % Calcd.	Found	
CH_3	$CH_2C_6H_5$	$C_{12}H_{14}ON_2$[a]	142–143	13.86	13.78	13.81
C_2H_5	$CH_2C_6H_5$	$C_{13}H_{16}ON_2$[b]	86– 87	12.96	12.97	
C_2H_5	$CH_2CH_2C_6H_5$	$C_{14}H_{18}ON_2$[c]	116–118	12.17	12.29	

[a] Small colorless needles from toluene. [b] Colorless needles from benzene containing benzene of crystallization. [c] Colorless needles from water.

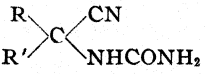
The Ureido-nitriles.—The method used by Read[5] for the preparation of ureido-nitriles from amino acid nitrile hydrochlorides was employed with slight modification in technique. The amino acid nitrile hydrochloride, suspended or dissolved in a suitable medium, is treated carefully with two equivalents of potassium cyanate. Read employed glacial acetic acid as a solvent for this reaction. We have also used this medium, but have found 50% acetic acid better suited in several cases. Moreover, we have found it necessary to neutralize the acetic acid with ammonia in order to obtain complete precipitation of the ureido-nitriles after the reaction mixture is diluted with water accord-

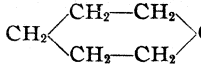
[11] Jawelow, *Ber.*, **39**, 1199 (1906).

[12] Smessarew, *J. prakt. Chem.*, **89**, 369 (1914).

ing to Read's procedure. The new ureido-nitriles prepared by us are recorded in Table III.

TABLE III

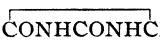


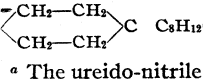
R	R′	Formula	M. p., °C.	N Analyses, % Calcd.	Found	Yield, %
CH_3	$CH_2C_6H_5$[a]	$C_{11}H_{13}ON_3$	170–171	20.59	20.47	86
C_2H_5	$CH_2C_6H_5$[b]	$C_{12}H_{15}ON_3$	124–126	19.35	19.22	91
CH_3	$CH_2CH_2C_6H_5$[a]	$C_{12}H_{15}ON_3$	138–142	19.35	19.38	83
C_2H_5	$CH_2CH_2C_6H_5$[b]	$C_{13}H_{17}ON_3$	139	18.18	18.15	93
		$C_8H_{13}ON_3$	180–181	25.14	25.15	92

[a] Glacial acetic acid medium for reaction. [b] 50% (volume) acetic acid medium for reaction.

Hydantoins from the Ureido-nitriles.—The formation of hydantoins from the corresponding ureido-nitriles is brought about by warming the nitriles in 20% hydrochloric acid solution, from which the hydantoins precipitate on forming. These are purified by recrystallization from 50% alcohol, from which they usually separate as colorless needles or prisms. The new hydantoins prepared by us are recorded in Table IV.

TABLE IV



R	R′	Formula	M. p., °C. (corr.)	Analyses, % Calculated C	H	N	Found C	H	N		Yield, %
CH_3	$CH_2C_6H_5$	$C_{11}H_{12}O_2N_2$	227–228	64.67	5.93	13.73	64.51	5.75	13.77	13.87	92
C_2H_5	$CH_2C_6H_5$	$C_{12}H_{14}O_2N_2$	217–218	66.01	6.47	12.84	66.06	6.28	12.87	12.91	72
CH_3	$CH_2CH_2C_6H_5$[a]	$C_{13}H_{14}O_2N_2$	179–180	66.01	6.47	12.84	66.05	6.51	12.92	12.67	82
C_2H_5	$CH_2CH_2C_6H_5$	$C_{13}H_{16}O_2N_2$	198–199	67.20	6.95	12.07	67.41	6.80	11.96	11.97	75
		$C_8H_{12}O_2N_2$	217–218	57.10	7.19	16.67	57.26	7.15	16.59	16.76	77

[a] The ureido-nitrile corresponding to this hydantoin melts under hot aqueous hydrochloric acid, and does not dissolve completely, hence the mixture should be stirred vigorously during heating to ensure complete reaction.

5,5-Cyclopentamethylenehydantoin crystallizes from 50% alcohol with one molecule of water of crystallization, which is lost on heating to 105–110°. The following analysis was made on a sample dried to constant weight at 105–110°.

Anal. Calcd. for $C_8H_{12}O_2N_2 \cdot H_2O$: H_2O, 9.67. Found: H_2O, 9.48.

Salts of the Hydantoins with Metals.—The sodium salts of the above hydantoins are easily prepared by treating a small amount of the hydantoin with the calculated quantity of a 5% solution of sodium hydroxide in 95% alcohol. On evaporating the alcohol in a vacuum desiccator, the sodium salt of the hydantoin remains as a colorless, crystalline residue. These salts are very soluble in water, slightly soluble in 95% alcohol, and insoluble in most other organic solvents. Acetic or mineral acids, and carbon dioxide precipitate the hydantoins from aqueous solutions of their sodium salts. Aqueous solutions of the sodium salts absorb carbon dioxide from the air with subsequent precipitation of the free hydantoins. However, the sodium salts are quite stable in aqueous solution when carbon dioxide is excluded. A water solution of the sodium

salt of nirvanol[13] was kept for six weeks in a sealed tube at 40–50°, after which the hydantoin was recovered almost quantitatively on addition of carbon dioxide.

The mercury salts of the hydantoins precipitate as flocculent, colorless solids when a saturated solution of mercuric chloride is added to aqueous solutions of the sodium salts of the hydantoins. Similarly crystalline calcium and magnesium salts of the hydantoins precipitate when strong solutions of calcium chloride and magnesium sulfate, respectively, are added to aqueous solutions of the hydantoin sodium salts.

α-Amino-α-phenylbutyric Acid, $C_6H_5C(C_2H_5)(NH_2)COOH$.—This amino acid was obtained by Jawelow[11] from propiophenone through the action of ammonium cyanide, followed by hydrolysis of the amino acid nitrile formed. His description of the compound is limited to the statement that it separates from water in groups of needles. We have prepared this same amino acid by hydrolyzing phenylethylhydantoin with barium hydroxide.

A mixture of 10 g. of the hydantoin, 50 g. of crystallized barium hydroxide, and 100 cc. of water is refluxed for one hundred hours, when the evolution of ammonia will have practically ceased. The excess of barium hydroxide is precipitated as the carbonate by bubbling carbon dioxide into the mixture. After filtering off the barium carbonate and washing with hot water, the combined filtrate and washings are concentrated until the amino acid begins to crystallize from the solution. On cooling, α-amino-α-phenylbutyric acid separates in the form of clusters of needles. The amino acid is purified by dissolving in dilute ammonia water, and concentrating on the steam-bath until crystallization begins. A yield of 79 g. of the amino acid, melting at 275° (corr.) with charring, was obtained.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.00; H, 7.32; N, 7.82. Found: C, 67.09; H, 7.25; N, 7.50, 7.50.

The compound shows all the characteristic properties of an α-amino acid. It is soluble in hot water and glacial acetic acid, slightly soluble in cold water and insoluble in most other organic solvents.

Hydrochloride.—This is a colorless, crystalline solid, very soluble in water and melting at 271° (corr.) with charring and effervescence.

Anal. Calcd. for $C_{10}H_{14}O_2NCl$: N, 6.50; Cl, 16.47. Found: N, 6.62; Cl, 16.76.

α-Phenylureido-α-phenylbutyric Acid, $C_6H_5C(C_2H_5)(NHCONHC_6H_5)COOH$, crystallizes from 75% alcohol in small, colorless needles, melting at 190–190.5° (corr.) with complete disappearance of all the material.

Anal. Calcd. for $C_{17}H_{18}O_3N_2$: N, 9.40. Found: N, 9.60.

α-Amino-α-methyl-β-phenylpropionic Acid, $C_6H_5CH_2C(CH_3)(NH_2)COOH$.—This amino acid was prepared from 5-methyl-5-benzylhydantoin in the same manner as that described for α-amino-α-phenylbutyric acid. In this case the hydantoin is completely broken down after thirty hours of boiling with barium hydroxide solution. It crystallizes from water in bunches of colorless needles, melting at 293–294° (corr.) with charring.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.00; H, 7.32; N, 7.82. Found: C, 66.90; H, 7.18; N, 7.76.

This compound has about the same solubility in various solvents as its isomer, α-amino-α-phenylbutyric acid.

The hydrochloride is a colorless crystalline acid, melting at 244–246° (corr.) with charring and gas evolution.

Anal. Calcd. for $C_{10}H_{14}O_2NCl$: N, 6.50; Cl, 16.47. Found: N, 6.44, 6.46; Cl, 16.49.

[13] Prepared according to Read's method, Ref. 5.

α-Phenyl-ureido-α-methyl-β-phenylpropionic Acid, $C_6H_5CH_2C(CH_3)(NHCONHC_6H_5)COOH$, crystallizes from 50% alcohol in small, colorless prisms, melting at 187° (corr.) with complete disappearance of the material.

Anal. Calcd. for $C_{17}H_{18}O_3N_2$: N, 9.40. Found: N, 9.49.

Pharmacological Report

The results of a preliminary pharmacological examination of the above hydantoins are summarized in Table V, compiled from a report kindly submitted by Mr. C. L. Rose,[14] of the Lilly Research Laboratories, Indianapolis, Indiana. The hypnotic value of the compounds was tested in the usual manner, by intraperitoneal injection of white rats with a definite volume dose of the material to be tested. The doses were measured in milligrams per kilogram of rat weight, and the results read in terms of dosage, as, Minimum Hypnotic Dose (M. H. D.), Maximum Tolerated Dose (M. T. D.), Minimum Lethal Dose (M. L. D.), and the safety factor or Ratio of M. H. D. to M. T. D.

TABLE V

PHARMACOLOGICAL BEHAVIOR

Compound	M. H. D.	M. T. D.	M. L. D.	Ratio
Ethylphenylhydantoin (nirvanol)	165	190	200	1.21
Methylbenzylhydantoin	550	650	700	1.28
Ethylbenzylhydantoin	500	450	500	1.00
Methyl-β-phenylethylhydantoin	250	500	550	2.20
Ethyl-β-phenylethylhydantoin	275	390	400	1.45
Cyclopentamethylenehydantoin	None	150	200	...

Discussion of the Pharmacological Data

5-Methyl-5-β-phenylethylhydantoin stands out as the best hypnotic of the group. It is less than half as toxic as nirvanol, and its effective dose somewhat approaches that of nirvanol, while its margin of safety is nearly twice that of nirvanol. Next best is 5-ethyl-5-β-phenylethylhydantoin, which is only 9% less effective and 27% more toxic than its methyl analog.

Although 5-methyl-5-benzylhydantoin is 21% less toxic than 5-methyl-5-β-phenylethylhydantoin, it must be ruled out because of the convulsions it causes in low doses. 5-Ethyl-5-benzylhydantoin is but 9% more toxic than 5-methyl-5-β-phenylethylhydantoin, but it is not effective outside the toxic range. 5,5-Cyclopentamethylenehydantoin has about the same toxicity as nirvanol, but has no effective range and causes a considerable increase in the activity of the salivary gland. Several of these new hydantoins of the nirvanol type are now being tested clinically by different medical investigators.

The authors desire to acknowledge the assistance of Mr. W. Saschek of the Department of Biochemistry, Columbia Medical School, New York

[14] The authors desire to express here their appreciation of the assistance given by the Lilly Research Laboratories in carrying out these preliminary pharmacological tests.

City, who made the microanalyses for carbon and hydrogen, which are reported in this paper.

Summary

1. A series of new 5,5-dialkyl-hydantoins has been prepared.
2. A report of a preliminary pharmacological study is included.
3. Several of these hydantoins, 5-methyl-5-β-phenylethylhydantoin, and its 5-ethyl analog, have marked hypnotic properties, and are being subjected to clinical study to determine whether they possess any therapeutic value in the treatment of nervous diseases.
4. Two new α-amino acids related to the hydantoins have been prepared.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE DIRECTIVE INFLUENCE OF THE ALKYLSULFONAMIDO AND DIALKYLSULFONAMIDO GROUPS

BY R. L. SHRINER, M. T. GOEBEL AND C. S. MARVEL

RECEIVED FEBRUARY 1, 1932 PUBLISHED JUNE 6, 1932

There have been numerous attempts to formulate rules which will allow one to predict the position which a group will take when it enters a monosubstituted benzene ring. Interest in this general problem has been revived by the appearance of two papers[1] which set forth new empirical rules which are apparently less subject to exceptions than are the previous generalizations. It is obvious, however, that a general rule based on theoretical considerations cannot be formulated until all of the common substituents in the ring have been considered. The present work concerns the sulfonamido and disulfonamido groups, which have not been fully considered in the earlier papers.

Hammick and Illingworth[1b] have stated the following orientation rule: "If in the benzene derivative C_6H_5XY, Y is to the right of X in the periodic table, or if, being in the same group, Y is of a lower atomic weight than X, a second atom or group will enter the nucleus in the meta position. In all other cases including that in which XY is a single atom, a second entering group or atom goes to the ortho and para positions." The effect of ionic charges on XY is also discussed and it is pointed out that positive charges direct meta and negative charges direct ortho and para. In the application of their rule they do not clearly indicate what may be expected from a group such as CH_2Cl or $CHCl_2$ where X is C and Y may be H or Cl. In such a case it is obvious that following the rule alone one would predict mixtures of ortho, meta and para isomers. This agrees

[1] (a) Latimer and Porter, THIS JOURNAL, **52**, 206 (1930); (b) Hammick and Illingworth, *J. Chem. Soc.*, 2358 (1930). A review of the earlier literature can be found in these articles.

fairly well with the facts which have been established by experiment. A group such as the sulfonamido $-N\langle^{SO_2R}_{H}$ is another of this doubtful type, for the hydrogen atom is to the left of the nitrogen in most arrangements of the periodic table and sulfur is to the right of nitrogen. Hence, according to the above rule, a mixture of all three isomers would be predicted. Another factor which must be considered is the acidic properties of the monosulfonamides. This property would lead one to expect a behavior similar to that of the aci-nitro compounds which, as Baker[2] has shown, direct the entering group meta.

However, the aryl sulfonamido group is known to be a group which directs mainly to the ortho and the para positions. Without attempting to cite all of the literature references it can be stated that many aryl sulfonanilides have been halogenated and nitrated and that the products formed were ortho and para substituted derivatives. Quite recently Bell[3] has studied carefully the nitration and halogenation of certain aryl sulfonanilides and has compared the directive effect of the aryl sulfonamido group with that of the acetamido group. His results indicate clearly that the aryl sulfonamido group is an ortho–para directing group.

The disulfonamido group $-N-(SO_2R)_2$ has been less thoroughly examined and the only information concerning its effect is the statement by Bell[3b] that it is more difficult to nitrate a diaryl sulfonanilide than an aryl sulfonanilide and that under vigorous conditions of nitration nitro groups are introduced in both the aryl sulfonyl and the aniline residues. The rule of Hammick and Illingworth[1b] would lead one to predict that the disulfonamido group would direct an entering group to the meta position only.

Latimer and Porter[1a] base their predictions of the position taken by a group entering a monosubstituted benzene ring on values obtained by calculating in a semi-quantitative manner the residual charge on the atom attached to the ring. By a study of most of the known groups they show that if the residual charge on this atom has a high positive value ($>+0.6$), the new group enters the meta position; whereas if the value of the residual charge is negative, zero or slightly positive ($<+0.1$), ortho and para substitution occur. Mixtures result in the case where the residual charge is between $+0.1$ and $+0.6$. If Latimer and Porter's method of calculating residual atomic charges is applied to the sulfonamido and disulfonamido groups the results are as follows

Residual charge on nitrogen equals

$$C_6H_5:\ddot{N}(H):\ddot{S}O_2R \quad +5-2-(2\times{}^1/_2)-(2\times{}^5/_9)-(2\times{}^5/_{11})=-0.02$$

[2] Baker, *J. Chem. Soc.*, 2257 (1929).

[3] Bell (a), *ibid.*, 2770 (1928); (b) 2787 (1929); (c) 2338 (1931).

Residual charge on nitrogen equals

$$C_6H_5:\ddot{N}(SO_2R)(\ddot{S}O_2R) \quad +5-2-(2\times{}^5/_9)-(4\times{}^5/_{11})=+0.07$$

It will be noted that the charge on the nitrogen atom is negative in the monosulfonanilide, and slightly positive but less than +0.1 in the disulfonanilide. Hence, both of these groups would fall in the ortho and para directing class.

The present work was undertaken to confirm the previously reported directive effects of the sulfonamido group and to determine that of the disulfonamido group. Methanesulfonanilide and dimethanesulfonanilide were selected for study because each contains only one aromatic nucleus and the alkyl sulfonyl group is small so that steric effects should be of less consequence. Nitration was selected as a suitable reaction for introducing a new group since it is a characteristic reaction and usually gives crystalline derivatives. The nitration of methanesulfonanilide proceeded smoothly and the crystalline product isolated from the nitration mixture in yields of over 80% of the theoretical amount was 2,4-dinitro-methanesulfonanilide. Some hydrolysis occurred during nitration. Hydrolysis and mechanical losses account for the difference between the actual yield and the theoretical yield. No other isomer could be detected.

The nitration of dimethanesulfonanilide was more difficult to bring about. The fact that nitration proceeded more slowly was in agreement with the statement of Bell[3b] concerning substitution in diaryl sulfonanilides. In addition to the well-defined crystalline *p*-nitro derivative, a mixture of lower-melting products, including a resinous impurity, was obtained. The lower-melting fractions were hydrolyzed and by steam distillation some *o*- and *m*-nitroanilines were carried over. A further quantity of *p*-nitroaniline was recovered in the non-volatile portion. By repeated distillation with steam and recrystallization, rather pure *m*-nitroaniline was obtained. A very small amount of crystalline *o*-nitroaniline was obtained by sublimation. With this evidence of its presence further estimation of the amounts of the ortho and meta isomers which were present in the material could be made by use of Tingle and Roelker's[4] data on the melting points of mixtures of these compounds.

The results of this separation of products indicate that the nitration of dimethanesulfonanilide gave over 61% of the para isomer, and approximately 13% of meta and 6% of the ortho isomers. This estimation of the ortho isomer is the least satisfactory and probably the portion unaccounted for was the ortho isomer. It is thus established that the di-methanesulfonamido group is essentially an ortho–para directing group.

[4] Tingle and Roelker, THIS JOURNAL, **30**, 822 (1908).

Experimental Part

Methanesulfonyl chloride and methanesulfonanilide were prepared by the procedures previously described.[5]

Dimethanesulfonanilide.—A solution of 27 g. of methanesulfonanilide and 20 g. of methanesulfonyl chloride in 100 cc. of dry benzene was refluxed for two hours. The solvent was then removed by distillation under reduced pressure and the sirupy residue was treated with about 200 cc. of cold 10% aqueous sodium hydroxide solution to extract the unreacted methanesulfonanilide. The insoluble residue was collected on a Büchner funnel and washed repeatedly with hot alcohol. The white crystalline material thus obtained weighed 29 g. (71% of the theoretical amount); m. p. 201–202°.

Anal. (Kjeldahl) Subs., 0.5032, 0.4420: 20.2, 17.6 cc. of 0.101 *N* HCl. Calcd. for $C_8H_{11}O_4NS_2$: N, 5.62. Found: N, 5.68, 5.64. (Parr Bomb) Subs., 0.6355, 0.3370: $BaSO_4$, 1.1969, 0.6317. Calcd. for $C_8H_{11}O_4NS_2$: S, 25.7. Found: S, 25.80, 25.67.

Nitration of Methanesulfonanilide.—To a well-stirred mixture of 100 cc. of concentrated nitric acid (sp. gr. 1.42) and 50 cc. of concentrated sulfuric acid (sp. gr. 1.84) maintained at 30–40° was slowly added 20 g. of methanesulfonanilide. The addition required an hour and the mixture was allowed to stand for three hours longer. It was then poured into 400 cc. of ice and water in order to precipitate the nitration product. By filtering this solution and air drying the precipitate, there was obtained 27 g. of light yellow product, m. p. 120–170°. This product was washed four times with 50-cc. portions of hot alcohol. The insoluble residue weighed 23 g. and melted sharply at 171–172°.

The alcoholic solution was evaporated and yielded 4 g. of a product melting at 130–160°. This was renitrated with 50 cc. of red fuming nitric acid at 40°. On working up this mixture as before 1.5 g. of product melting at 170–172° was obtained. From the alcoholic mother liquors about 1 g. of low melting material was again recovered.

Further recrystallization of the nitration product gave pure 2,4-dinitromethanesulfonanilide which melted at 173.5–174.5°.

Anal. (Parr Bomb). Subs., 0.6625, 0.6588: $BaSO_4$, 0.6000, 0.5945. Calcd. for $C_7H_7O_2SN(NO_2)_2$: S, 12.25. Found: S, 12.41, 12.36.

The total yield of dinitro compound (m. p. 170–172°) was 24.5 g. (80.6% of the theoretical amount). The fact that the low-melting compound could be further nitrated to yield the higher-melting compound indicated that the first product was a mixture of ortho- and para-mononitro derivatives.

Identification of the Dinitromethanesulfonanilide.—Five grams of the dinitromethanesulfonanilide (m. p. 170–172°) obtained as described above was hydrolyzed by refluxing it for six hours with a mixture of 30 cc. of concentrated sulfuric acid and 30 cc. of water. The reaction mixture was poured into a large volume of ice water and the precipitate of 2,4-dinitroaniline was filtered. After washing with water and alcohol and air drying, the yellow crystalline material melted at 176.5–178° and weighed 3.5 g. (practically a quantitative yield). A mixture of this product with known 2,4-dinitroaniline (m. p. 180°) melted at 179–180°.

The 2,4-dinitroaniline from the hydrolysis mixture was further characterized by treating a sample (0.5 g.) with excess acetyl chloride. The 2,4-dinitroacetanilide thus obtained melted at 119–120°. The melting point recorded for this product is 120–121°.

The same dinitromethanesulfonanilide was obtained by nitrating *p*-nitromethanesulfonanilide prepared by the method of Morgan and Pickard.[6]

[5] Marvel, Helfrick and Belsley, THIS JOURNAL, 51, 1272 (1929).

[6] Morgan and Pickard, *J. Chem. Soc.*, 97, 61 (1910).

Nitration of Dimethanesulfonanilide.—Preliminary experiments showed that nitration did not take place when dimethanesulfonanilide was treated with a mixture of concentrated nitric and sulfuric acid at 30–40°, or at 60–70°. The use of fuming nitric acid gave satisfactory results.

To a mixture of 100 cc. of red fuming nitric acid (sp. gr. 1.60) and 50 cc. of concentrated sulfuric acid (sp. gr. 1.84) was added slowly 30 g. of dimethanesulfonanilide. The mixture was stirred and the temperature maintained at about 20°. The mixture was stirred for two hours after the addition of the anilide was complete, diluted with ice water, and filtered. The crude air-dried nitration product weighed 30 g. (85% of the theoretical yield of mononitro compound).

Repeated extraction with hot alcohol and subsequent recrystallization yielded, from 24 g. of the crude product, the following fractions: (I) m. p. 215–225°, 12 g.; (II) m. p. 160-195°, 3 g.; (III) m. p. 140–150°, 5 g.; (IV) m. p. 110–135°, 1.5 g.; (V) resinous material, 1 g.

Fraction (I), which was almost insoluble in hot alcohol, was further washed, and finally recrystallized from benzene. The pure product melted at 230–231°. It was analyzed for sulfur and results of the analysis show that it is a mononitro derivative.

Anal. (Parr Bomb). Subs., 0.3985: $BaSO_4$, 0.6379. Calcd. for $C_8H_{10}O_4NS_2(NO_2)$; S, 21.77. Found: S, 21.91.

***p*-Nitrodimethanesulfonanilide.**—The structure of the compound constituting Fraction I was established by synthesis from *p*-nitromethanesulfonanilide and by hydrolysis to *p*-nitroaniline. One gram of *p*-nitromethanesulfonanilide was refluxed with 2 cc. of methanesulfonyl chloride and 2 cc. of tributylamine in toluene solution. The toluene was distilled under reduced pressure and the residue was washed with sodium carbonate solution and dilute hydrochloric acid. The insoluble residue (0.5 g.) was recrystallized from an excess of hot alcohol. The product melted at 225–228°. A mixture with the product obtained in fraction I above melted at 228–230°.

Hydrolysis of Nitration Products.—Five grams of fraction (I) was refluxed for six hours with a mixture of 30 cc. of concentrated sulfuric acid and 30 cc. of water. The reaction mixture was cooled, diluted with water to 200 cc., made slightly alkaline by the addition of 20% sodium hydroxide solution, cooled and extracted with three 200-cc. portions of ether. The residue after evaporating the ether from the extract weighed 2.2 g. and melted at 141–145°. A mixed melting point with known *p*-nitroaniline showed no depression.

One gram of this product was refluxed with a slight excess of acetic anhydride for fifteen minutes. The *p*-nitroacetanilide, recovered by dilution with water, melted at 203–207°. The melting point of *p*-nitroacetanilide is given as 207–210°.

The lower melting fractions which remained after separating the pure *p*-nitrodimethanesulfonanilide could not be separated into pure substances by further crystallizations. No simple or accurate method of analysis was available but by the following methods it was possible to show that some meta- and some ortho-nitrodimethanesulfonanilide were formed in the nitration.

Two grams of fraction (II) was hydrolyzed with 50% sulfuric acid. This reaction mixture was then diluted, neutralized with sodium hydroxide solution, and steam distilled. Two liters of distillate were collected. Each portion of distillate was extracted with ether. Fraction (VI), recovered from the first liter of distillate as a residue when the ether was evaporated, weighed 0.1 g. and melted at 80–90°. Fraction (VII), recovered in the same manner from the second liter, weighed 0.2 g. and melted at 90–110°. The residue remaining in the distilling flask was also extracted with ether to yield fraction (VIII) which weighed 0.4 g. and melted at 135–141°. Fraction (VIII) when mixed with known *p*-nitroaniline melted at 140–145°.

Three grams of fraction (III) was hydrolyzed and the products of hydrolysis were separated as above. Fraction (IX) weighed 0.2 g. and melted at 55–80°. Fraction (X) weighed 0.2 g. and melted at 85–100°. Fraction (XI), recovered from the residue, melted at about 90°. It was recrystallized from alcohol and yielded 0.4 g. of material (fraction (XII)) melting at 127–139°. This was mainly *p*-nitroaniline. Fraction (XIII), recovered from the alcoholic mother liquors, weighed 0.2 g. and melted at 85–95°.

One gram of fraction (IV) was hydrolyzed as described above. It was then extracted with ether. The material recovered from this extract weighed 0.4 g. and melted at 48–80°. This residue was not entirely soluble in dry ether, however. About 0.05 g. was recovered as an insoluble residue, melting above 260°, which burned explosively when held over the Bunsen flame. This product was isolated in only one experiment, and so could not be investigated further. The ether-soluble portion now melted at 48–70°.

Fractions (VI), (VII), (X), and (XIII) were combined and dissolved in 10 cc. of dilute hydrochloric acid. This solution was made slightly alkaline. On long standing, and cooling in an ice-bath, 0.4 g. of material precipitated out as yellow needle-like crystals, melting at 108–112°. A mixed melting point with known *m*-nitroaniline (m. p. 114°) showed no depression.

The *m*-nitroacetanilide was prepared by treatment with acetic anhydride and melted at 147–149°. This checks the melting point reported for *m*-nitroacetanilide.

Fraction (IX) was combined with the low melting product recovered by hydrolysis of fraction (IV). This was placed in a porcelain dish, covered with a watch-glass, and allowed to stand for several days. At the end of this time, 0.1 g. of sublimate was recovered from the watch-glass. This material melted at 65–68°, and melted at 67–70° when mixed with known *o*-nitroaniline.

By this rather complicated method, from 24 g. of nitration product there was recovered 12 g. of substantially pure *p*-nitrodimethanesulfonanilide and 1.25 g.[7] of *p*-nitroaniline. This corresponds to 61% of the theoretical amount of *p*-nitro isomer.

There was also isolated 1.1 g. of impure *m*-nitroaniline which melted 87–104°. Tingle and Roelker[4] have found that a mixture of nitroanilines containing 20–22% of the ortho isomer and 80–78% of the meta isomer melts in this range. In calculating the approximate yields of the isomers formed in our experiments, this mixture was assumed to contain 20% of the ortho isomer.

A further fraction of 0.95 g. of a mixture of *o*- and *m*-nitroanilines melting from 60–80° was obtained. The melting point curves indicate that the mixtures of the ortho and meta isomers which melt in this range contain about 40% of the ortho compound. This figure was used in calculating the composition of this fraction.

This indicates that the original nitro derivative contained approximately 13% of meta and 6% of the ortho isomer. These figures represent the minimum amounts of each which must have been formed during the nitration of dimethanesulfonanilide.

Summary

1. The nitration of methanesulfonanilide results in an 80% yield of 2,4-dinitromethanesulfonanilide.

2. The nitration of dimethanesulfonanilide yields a mixture of mononitro derivatives which have been shown to contain at least 61% para, 13% meta and 6% ortho. The estimation of the ortho isomer is the least satisfactory.

[7] This figure is calculated as the total amount of *p*-nitroaniline and is based on the results of the hydrolysis of an aliquot part of fraction (VI).

3. These results indicate that the directive effect of the monosulfonamido and disulfonamido groups in the benzene ring is predominantly ortho–para.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

THE PREPARATION OF CERTAIN KETO-CHLORIMINES BY THE ACTION OF CHLORINE ON COMPOUNDS OF THE TYPE R′R″C=NMgX[1]

BY C. R. HAUSER, H. A. HUMBLE AND G. J. HAUS

RECEIVED FEBRUARY 1, 1932 PUBLISHED JUNE 6, 1932

In connection with a study of ald-chlorimines[2] we were desirous of obtaining certain keto-chlorimines in order to make a comparative study of these compounds. Several keto-chlorimines previously have been prepared by Peterson[3] by a method which involves several steps. Thus, benzophenone was converted into benzophenone dichloride, which in turn was converted, by means of urethan, into the imine hydrochloride. The latter was treated with hypochlorous acid, yielding the chlorimine according to equation (1).

$$(C_6H_5)_2C{=}NH + HOCl \longrightarrow (C_6H_5)_2C{=}NCl + H_2O \qquad (1)$$

In the hope of developing a shorter method for the preparation of certain keto-chlorimines, it seemed worth while to attempt the chlorination of nitrogen-magnesium compounds of the type R′R″C=NMgX,[4] which may readily be obtained from Grignard reagents and nitriles,[5] by means of chlorine (2), and of alkyl hypochlorites (3).

$$—R'R''C{=}NMgX + Cl_2 \longrightarrow R'R''C{=}NCl + MgXCl \qquad (2)$$

$$—R'R''C{=}NMgX + R'''OCl \longrightarrow R'R''C{=}NCl + MgXOR''' \qquad (3)$$

Since Durand and Naves[6] have shown previously that ethyl hypochlorite reacts with the nitrogen–magnesium compound obtained from aniline and ethylmagnesium bromide to yield presumably a chloramine (4), it might

$$—C_6H_5NHMgBr + C_2H_5OCl \longrightarrow C_6H_5NHCl + C_2H_5OMgBr \qquad (4)$$

[1] This paper is in part constructed from portions of a thesis presented by G. J. Haus in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of Arts and Sciences, Duke University.

[2] Hauser and Gillaspie, THIS JOURNAL, **52**, 4158, 4517 (1930).

[3] Peterson, *Am. Chem. J.*, **46**, 325 (1911).

[4] Since compounds of the type R′R″C=NMgX might be considered as salts of imines (R′R″C=NH) and MgX(OH), chlorine might be expected to react with the nitrogen–magnesium linkage under certain conditions. Doubtless other reactions also occur. A discussion of these reactions is withheld pending further investigation.

[5] Blaise, *Compt. rend.*, **132**, 40 (1901).

[6] Durand and Naves, *Bull. soc. chim.*, **37**, 717 (1925).

be expected that under certain conditions a chlorimine could be prepared according to equation (3). In this work *tert.*-butyl and *tert.*-amyl hypochlorites have been used since these are far more stable than either primary or secondary hypochlorites.[7]

It has been found that when diphenylmethylene-iminemagnesium bromide, obtained from phenylmagnesium bromide and benzonitrile, is treated with an equivalent quantity of chlorine or tertiary alkyl hypochlorite, an orange-red color develops and, after filtering and removing the ether, a red product is obtained which apparently contains about 60% of benzophenone chloramine as calculated from its active chlorine content. The pure chlorimine has not yet been isolated but its presence is further indicated by the fact that when the crude product in ether or benzene solution is treated with dry hydrogen chloride, a precipitate is obtained, which, presumably, is benzophenone-imine hydrochloride,[8] since benzophenone is obtained on hydrolysis.

The action of chlorine on the nitrogen-magnesium compound obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*-chlorobenzophenone chlorimine, which has a melting point of 104°, agreeing with that of the higher melting stereoisomer obtained by Peterson.[3] None of the lower melting stereoisomer has been found.

The action of chlorine on the nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*,*p'*-dichlorobenzophenone chlorimine.

Further work is in progress.

Experimental

Preparation of Tert.-Butyl and Tert.-Amyl Hypochlorites.—These hypochlorites were prepared by the method of Chattaway and Brackenberg.[7] The tertiary alcohol (1 mol) was added to a strong solution of sodium hydroxide (2 mols) and the resulting mixture diluted with water until a clear, homogeneous solution was obtained. After transferring to a brown bottle, the solution was cooled in an ice-bath and chlorine passed in as long as it was freely absorbed. The alkyl hypochlorite collected on the surface as a yellow oil and, after separating, was dried quickly with three successive portions of calcium chloride by shaking with the latter for a few seconds and then pouring the hypochlorite onto fresh calcium chloride, keeping the substance cold throughout the procedure. Eastman's *tert.*-butyl and *tert.*-amyl alcohols were used in this work. It was found that practical *tert.*-butyl alcohol gave a hypochlorite which decomposed within a short time.

Preparation of Nitrogen-Magnesium Compounds of the Type R'R"C=NMgX.—These compounds were prepared by Blaise's method.[5] The calculated amount of nitrile dissolved in ether was added to an ether solution of a Grignard reagent and the mixture warmed to complete the reaction. In our first experiments the amount of nitrile used

[7] Chattaway and Brackenberg, *J. Chem. Soc.*, **123**, 3000 (1923).

[8] Peterson has converted this imine hydrochloride into the chlorimine by means of hypochlorous acid (see eq. (1)).

was calculated by assuming a 75% yield of the Grignard reagent, but generally the reagent was analyzed by the acid titration method,[9] and the calculated amount of nitrile added, assuming that the substances react mole for mole. Sufficient Grignard reagent was always prepared so that one-eighth to one-quarter mole quantities of the nitrile were required in the preparation of the nitrogen-magnesium compound. The latter, which partially precipitated from the ether solution (volume about 150 to 300 cc.), was generally chlorinated as a suspension in this solvent, avoiding excess chlorine. In a few cases when the ether was first evaporated and benzene added, practically the same results were obtained.

Reaction of Tert.-alkyl Hypochlorites and of Chlorine with the Compound $(C_6H_5)_2$-C=NMgBr.—To a suspension in ether of the nitrogen-magnesium compound, obtained from phenylmagnesium bromide and benzonitrile, was added slowly with shaking an equivalent[10] amount of cold ether solution of *tert.*-butyl or amyl hypochlorite, cooling the reaction mixture in an ice-bath throughout the procedure. An orange-red color developed. After shaking vigorously for several minutes[11] the mixture was rapidly filtered with suction and the ether solution allowed to evaporate or distilled from a water-bath. A red oily residue with only a slight odor was obtained which was found to contain 10 to 11% of active chlorine. Calculated from its active chlorine content[12] the product contained more than 60% of benzophenone chlorimine. Yields were generally about 50% of crude product or about 30% of the chlorimine calculated from the benzonitrile used.

Similar results were obtained when the nitrogen-magnesium compound suspended in ether or benzene was treated with an equivalent of chlorine instead of the hypochlorite as described above. No hydrogen chloride was observed. After filtering rapidly the solvent was evaporated under vacuum by drawing the air through a calcium chloride drying tower. It had been found that when the red ether solution of the crude chlorimine was shaken with cold dilute sodium hydroxide, a yellow emulsion was produced which finally separated into two yellow layers. When the ether layer was dried and evaporated a lighter colored oily residue was obtained which contained about 10% of active chlorine; when the alkaline layer was acidified a few drops of red oil separated, which is being further studied.

Attempts thus far to obtain the pure chlorimine[13] by recrystallization of the crude products, obtained by both methods described above, have been unsuccessful. Oils which contained a slightly higher percentage of active chlorine and small quantities of crystals which contained no active chlorine were obtained.

A portion of the crude chlorimine (5 g.) in ether (100 cc.) was shaken with dilute sulfuric acid, then washed with water, shaken with dilute potassium hydroxide and again washed with water. After drying by shaking with calcium chloride in the cold, the

---

[9] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923); Gilman, Zoellner and Dickey, *ibid.*, **51**, 1577 (1929).

[10] The amount of hypochlorite used was equivalent to the amount of benzonitrile employed in the preparation of the nitrogen-magnesium compound.

[11] In several cases when the reaction mixture was allowed to stand at room temperature for several hours before filtering, practically the same results were obtained.

[12] The analysis for active chlorine was carried out by dissolving a sample in acetic acid, adding potassium iodide, and titrating with sodium thiosulfate, or by the method recently used for ald-chlorimines.[2]

[13] Benzophenone chlorimine (m. p. 37°) has been prepared by Peterson.[3] Since we were especially desirous of obtaining the chloro substituted chlorimines described in this paper, no further attempt has been made to isolate benzophenone chlorimine.

ethereal solution was saturated with dry hydrogen chloride. A precipitate was obtained which when warmed with water yielded benzophenone. When repeated without extracting with acid and alkali, similar results were obtained. When the acid extract, which had been separated from the ether solution of the crude chlorimine described above, was made alkaline, a trace of an organic solid was obtained, and when the alkaline extract was acidified, a small amount of red oil was obtained.

Preparation of *p*-Chlorobenzophenone Chlorimine.—To a suspension in ether of the nitrogen-magnesium compound, obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile, was added slowly with shaking the calculated amount of chlorine, keeping the mixture cold throughout the procedure. An orange-red color developed, being the darkest when approximately the calculated amount of chlorine had been added. After shaking vigorously, the mixture was filtered rapidly with suction and the ether solution either evaporated directly or first extracted with dilute sodium hydroxide, dried rapidly with calcium chloride, and then evaporated using a drying tower as described above. If the extraction with alkali is carried out carefully by shaking just sufficiently to remove the red color and yet not produce a heavy emulsion, the crude chlorimine obtained by the evaporation of the ether is generally a purer product having a lighter color, but the yield is smaller. The yield of chlorimine calculated from the nitrile used in the preparation of the nitrogen-magnesium compound was about 32% as calculated from the active chlorine content of the crude product. Two recrystallizations from ligroin or chloroform yielded white crystals melting at 104°, agreeing with the melting point of the higher melting stereoisomer obtained by Peterson.[3] Analysis for active chlorine gave the following result.

Anal. Calcd. for $ClC_6H_4 \cdot C_6H_5C{=}NCl$: Cl, 14.18. Found: Cl, 14.13.

An attempt was made to isolate a stereoisomer by following the procedure by which Peterson[3] isolated an isomer melting at 56°, but when a chloroform–ligroin solution of the product, from which a portion of the higher melting isomer had been separated, was cooled to −12°, more of the same isomer was obtained, and even after evaporating almost all of the solvent the substance obtained melted above 100°. None of the lower melting isomer was found. Since the precipitate obtained by filtering the ethereal reaction mixture yielded *p*-chlorobenzophenone when treated with acid, it appeared as if some of the suspension of the nitrogen-magnesium compound had not reacted with the chlorine, yet when a portion of this same precipitate was again suspended in ether or benzene and treated with more chlorine, only a small additional amount of product was obtained which contained active chlorine. When the preparation was carried out using sufficient ether to keep the nitrogen-magnesium compound in solution, about the same yield of chlorimine was obtained.

Preparation of *p,p'*-Dichlorobenzophenone Chlorimine.—The nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile was treated with chlorine as described in the preparation of *p*-chlorobenzophenone chlorimine. An orange color developed which, after filtering, was not entirely removed from the ether solution of the chlorimine by shaking carefully with dilute sodium hydroxide. When the ether was evaporated a red residue was obtained. When the latter was treated with hot ligroin, most of the red material dissolved, leaving a slightly colored crystalline solid, and when the ligroin solution was cooled, more of the slightly colored crystalline solid was obtained. After recrystallization from hot ligroin an analysis showed that the substance contained 11.86% of active chlorine; the theoretical amount, calculated for *p*-dichlorobenzophenone chlorimine, is 12.47% active chlorine. The yield was about 35–40% calculated from the nitrile used for the preparation of the nitrogen-magnesium compound. Further recrystallization from ligroin yielded white prisms, melting at 74° and containing 12.05, 12.06% active chlorine.

Summary

1. Certain keto-chlorimines have been prepared by the action of chlorine on nitrogen-magnesium compounds of the type R′R″C=NMgX, which may readily be obtained from Grignard reagents and nitriles.

2. The action of chlorine on the nitrogen-magnesium compound obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*-chlorobenzophenone chlorimine, m. p. 104°. No stereoisomer has been isolated.

3. The action of chlorine on the nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*,*p*′-dichlorobenzophenone chlorimine, m. p. 74°.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THOMAS AND HOCHWALT LABORATORIES, INC.]

POLYMERIZATION OF DIOLEFINS WITH OLEFINS. I. ISOPRENE AND PENTENE-2

BY CHAS. ALLEN THOMAS AND WM. H. CARMODY

RECEIVED FEBRUARY 2, 1932 PUBLISHED JUNE 6, 1932

When anhydrous aluminum chloride is placed with pure isoprene in which there is no appreciable amount of olefin present, and the mixture shaken, there is no temperature rise or any other obvious chemical reaction even when a considerable portion of anhydrous aluminum chloride has been added. Upon prolonged standing slow polymerization takes place, producing mainly the insoluble polymer described below. If to this mixture a small amount of olefin, such as pentene-2 or trimethylethylene, is added and the mixture shaken, an obvious reaction starts immediately which becomes violent if much of the olefin has been added, and unless the mixture is cooled the products will soon boil away. This interesting reaction, some phases of which were also observed and discussed by Aschan,[1] has led to the following investigation.

If an equimolar mixture of isoprene and pentene-2 or trimethylethylene is diluted with an inert hydrocarbon solvent and the mixture cooled with constant stirring, there can be added portion-wise small amounts of anhydrous aluminum chloride. After several hours a point is reached where there is no more evolution of heat. From the reaction mixture there is obtained, after decomposition of the aluminum chloride complex, two organic polymers, one soluble, the other insoluble in hydrocarbon solvents.

Soluble Polymer.—This polymer ranges from a viscous oil to a hard resin, depending upon the proportions of the olefin and diolefin employed and the subsequent treatment to which the product is subjected. The

[1] Aschan, *Chem. Abstracts*, **14**, 3823 (1916); *Ofversigi Finska Vetenskaps Soc.*, **58**, 42 (1916).

product consists of a mixture of higher oils and a hydrocarbon resin, the hardness depending upon the amount of oils removed. The color of the resin ranges from light straw to dark brown, the darker color resulting from elevated or prolonged heating in removing the associated oils. If low boiling inert solvents are used, such as hexane, a harder resin can be obtained with less heating as the solvent can be taken off at a lower temperature and its high vapor pressure helps to distil the associated oils. The resin is soluble in most hydrocarbon solvents such as gasoline, benzene, toluene, chlorinated hydrocarbon solvents, and drying oils such as linseed and china wood oil. It is virtually insoluble in ethyl and methyl alcohol and acetone and can be precipitated out of the hydrocarbon solution by them. It is also difficultly soluble in ethyl acetate but appreciably soluble in the higher acetates such as butyl and amyl. It has been found that when this resin polymer is exposed in a thin film to air it slowly oxidizes, becoming harder upon oxidation. A thin film was obtained by flowing on a glass plate a solution of the resin polymer in benzene and allowing the solvent to evaporate, and the iodine and acid numbers of portions of the film were taken and recorded daily. Initially the iodine value was 202 and the acid value 0.4, but after twenty-seven days the iodine value had irregularly fallen to 136 and the acid number risen to 16. After this apparently an equilibrium was reached and the polymer did not change appreciably. Ozone is absorbed rapidly at first when bubbled through a solution of this polymer in carbon tetrachloride, the absorption slowing down and finally stopping, yet the iodine number of the solution in some cases was as high as 140. If the carbon tetrachloride is distilled off there remains a brittle amorphous yellow solid which is now insoluble in carbon tetrachloride. This indicates that further polymerization has taken place during the heating to remove the solvent.

Insoluble Polymer.—This polymer occurring with the residue filtered from a solution of the above-described soluble polymer is freed from inorganic matter by repeatedly digesting and washing with 10% hydrochloric acid and water. There remains on drying at low temperatures, a white, granular organic polymer which by combustion was proved to conform to the formula $(C_5H_8)_x$. No molecular weight has yet been determined, as this polymer is characterized by its extreme insolubility, having been found insoluble in the solvents tried, with the exception of nitrobenzene and some of the higher amines in which it is only very slightly soluble. Strong acids decompose the product and phenols react giving a reddish-violet coloration with decomposition. This polymer begins to depolymerize when heated to around 116°. It first contracts, becoming more spongy and rubbery, and changes to a tan or brown color with small globules of oil being formed. On continuing the heating to 299° the whole mass begins to fuse and slowly changes to a dark heavy oil with some foaming which on cooling

solidifies to a transparent dark resin which is soluble in most hydrocarbon and chlorinated hydrocarbon solvents.

By varying the amounts of olefin polymerized with the isoprene, under the conditions recorded below, various amounts of the two polymers can be obtained as shown in Fig. 1, in which pure pentene-2 was polymerized in varying molar amounts with a mole of isoprene. The ordinates of the

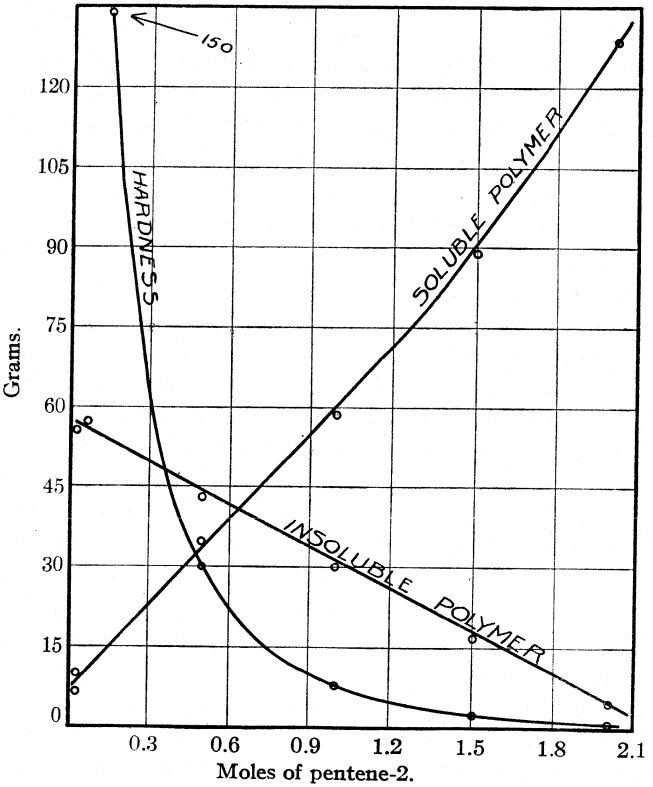


Fig. 1.—Yield of soluble and insoluble polymers formed when pentene-2 is varied, keeping isoprene constant at 1 mole. Variation in hardness of soluble polymer.

curve marked "Soluble Polymer" show the increase in grams of this polymer proportional to the pentene-2 used up to two moles, while the curve "Insoluble Polymer" shows the reverse relationship. When pentene-2 alone is polymerized with anhydrous aluminum chloride, no insoluble polymer is obtained, the product being an oil consisting of the various polymers of the olefin.[2] It appears therefore that the "Insoluble Polymer" curve approaches zero as a limit. The hardness of the soluble polymer is shown by

[2] F. W. Sullivan, Jr., V. Voorhees, A. W. Neeley and R. V. Shankland, *Ind. Eng. Chem.*, **23**, 604–611 (1931).

the lower curve, the ordinates of which are the reciprocals of the penetration value as measured by the A. S. T. M. penetration apparatus at 0° and 200 g. for sixty seconds, multiplied by 150. As can be seen, the hardness of the polymer rapidly decreases with the amount of pentene-2 in the mix. The product with two moles of the olefin is a heavy oil at the arbitrary end-point of hardening at 190°. By heating the product to a higher temperature or placing it under a vacuum, more of the oils can be distilled off, the polymer likewise being harder. However, if the temperature is taken too high, depolymerization starts as in the case of the insoluble polymer.

In this work no isoprene could be obtained which did not contain a small amount of olefin, so it is not known whether chemically pure isoprene polymerized under the prescribed conditions would give zero amount of soluble polymer. If this is the case, the whole "Soluble Polymer" curve would move down as the same isoprene was used for all points. The molecular weights on these soluble polymers vary from 845 to 1240 depending on the amount of lower polymers distilled from the resin. In general the more olefin present in the mixture, the lower the molecular weight. Likewise the combustions vary, the greater the amount of lower polymers removed, the closer the formula approaches to $(C_5H_8)_x$. Other diolefins and olefins give this characteristic reaction, the mechanism of which will be discussed in a later paper.

Experimental Procedure

The isoprene used was obtained by the destructive distillation of rubber, and the pentene-2 by dehydrating methylpropylcarbinol. The solvent was a paraffin hydrocarbon, boiling range 95–135°.

The mixture of isoprene, pentene-2 and solvent was carefully measured into a vessel equipped with a good agitator and cooled to 1°. At suitable intervals, depending on the temperature rise, approximately 0.8-g. portions of aluminum chloride were poured into the agitated mixture. When the reaction was nearly completed the catalyst was added in larger quantities, the temperature varying from 1 to 4°. The amount of aluminum chloride used was proportional to the isoprene and pentene-2 in the mix, 0.2 and 0.1 mole of aluminum chloride being used per mole of isoprene and pentene-2, respectively. The reaction mixture was agitated for twelve hours, after which an alcohol–aqueous ammonia mixture was used for neutralization and precipitation of the catalyst and insoluble polymer. The products were separated by filtration. The precipitate after digestion with 10% hydrochloric acid was washed well with water, dried and weighed. The filtrate was evaporated to recover the soluble polymer. When reduced to a small volume the solution was heated in an electric furnace at a uniform temperature of 190° for forty-five minutes.

Ossian Aschan, *Chem. Abstracts*, **14**, 3654 (1916); *Ofversigi Finska Vetenskaps Soc.*, **58**, 122 (1915). Ossian Aschan, *Ann.*, **324**, 1 (1902). Wallace H. Carothers, *Chem. Rev.*, **8**, 353 (1931) (includes bibliography of 254 references). Gustav Egloff, *et al.*, *J. Phys. Chem.*, **35**, 1825 (1931) (includes bibliography of 159 references). Engler and Routala, *Ber.*, **43**, 388–397 (1910); **42**, 4613–4620 (1909); **42**, 4620 (1909). Gangloff and Henderson, THIS JOURNAL, **39**, 1420 (1917).

Summary

1. Isoprene and pentene-2 react in the presence of anhydrous aluminum chloride to form two polymers, one insoluble, the other soluble in hydrocarbon solvents.

2. The amount of the soluble polymer formed is a function of the pentene-2 present. The hardness is an inverse function of the amount of pentene-2 present.

3. The amount of the insoluble polymer is an inverse function of the pentene-2 present.

DAYTON, OHIO

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF MIAMI UNIVERSITY]

ALKAMINE ESTERS OF AROMATIC ACIDS: NOVOCAINE ANALOGS. II[1]

BY HARVEY C. BRILL

RECEIVED FEBRUARY 5, 1932 PUBLISHED JUNE 6, 1932

A search of the chemical literature relating to the novocaine type of anesthetic reveals very few compounds of the type $-O(CH_2)_nN\begin{matrix}x\\y\end{matrix}$. A small number[2] have been made by comparison with the number of the type with identical substituents.

The difficulty of preparing secondary amines with dissimilar alkyl groups appears to have inhibited the investigative curiosity of workers in this field.

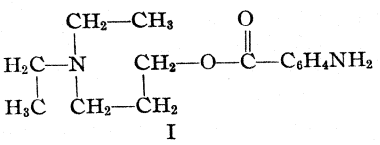
A study of the effects on the properties of the novocaine class of compounds of groups of this sort seemed worth while when the influence of such arrangements in the properties of the barbituric acid type of hypnotics, *e. g.*, Ipral, Amytal, Luminal, etc., is considered. In the absence of any considerable number of trustworthy generalizations that relate chemical

[1] Brill, THIS JOURNAL, **47**, 1134 (1925).

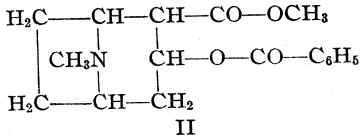
[2] (a) Volwiler and Adams, U. S. Patent 1,476,934 (Dec. 11, 1923), have made γ-butylallyl, γ-*n*-propylallyl, γ-isopropylallyl and γ-isoamylallylaminopropyl esters of benzoic acid; (b) v. Braun and Kirschbaum, *Ber.*, **52**, 2011 (1919), described a phenyl analog of novocaine, namely, the β-*p*-aminophenylmethylaminoethyl ester of *p*-aminobenzoic acid; (c) v. Braun and Braunsdorf, *ibid.*, **54**, 208 (1921), listed β-ethylallyl, β-ethylstyryl and β-ethylfuromethylaminoethyl esters of *p*-aminobenzoic acid; (d) Thorp has patented the hydrochloride of the benzoic ester of 1-methylethylamino-3-methylethylamino-2-hydroxypropane, U. S. Patent 1,193,649 (Aug., 1916). These compounds are reported to possess anesthetic properties.

structure and physiological activity, the only means of learning of the effects of such relationships is to prepare compounds of slight structural differences and study the effects of such changes.

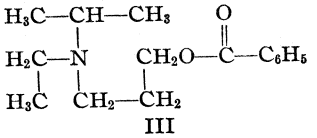
Kamm[3] has made the γ-diethylaminopropyl ester of *p*-aminobenzoic acid (I) and pointed out its structural similarity to cocaine (II). The structural resemblance between cocaine and γ-isopropylethylaminopropyl benzoate (III) appears more striking than between the pair pointed out by Kamm. This resemblance is really still more pronounced between (III) and tropacocaine (IV).



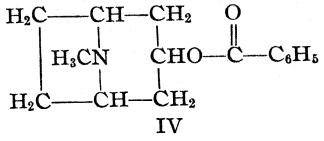
I



II



III



IV

If close similarity of structures between anesthetics of the novocaine type and cocaine or tropacocaine is conducive to high anesthetic activity, it should be worth while to study γ-isopropylethylaminopropyl benzoate. The hydrochloride of this ester in water solution is acid to litmus, and would be somewhat irritating to the tissues on this account. Such compounds are improved in their effects by lowering their acidity by the introduction of an amino group in the aromatic radical or by forming salts with acids that are weaker than hydrochloric or sulfuric.[4] Even when an aromatic group is substituted for one of the substituent alkyls in the amino, v. Braun and Kirschbaum[2b] found that these compounds possessed marked anesthetic properties, provided they were made basic by the introduction of amino groups. When the acidity is allowed to rise, however, the compound becomes irritating, as is evidenced by the properties of β-phenylethylaminoethyl benzoate, which has a numbing effect but is pepper-like in its irritation on the tongue.

Experimental Part

The hydrochlorides of these anesthetic compounds can be made readily by condensing a benzene solution of the acid chloride taken in about 10% excess of the theoretical amount with a benzene solution of the theoretical quantity of the amino alcohol. The reaction is completed by occasionally shaking and warming on a steam-bath under a reflux for several hours. White crystalline precipitates form during the heating or immediately on cooling.

[3] Kamm, THIS JOURNAL, **42**, 1030 (1920).

[4] Pope, British Patent 260,346 (July, 1925), preparation of borocaines; Watson Williams, *Lancet*, **1**, 16 (1926); Copeland and Notton, *Brit. Med. J.*, **11**, 547 (1925).

The mixed secondary amines are most readily prepared in the pure state by alkylating the mono-alkyl aniline by means of the alkyl halide under a reflux, warming for one to five hours on a steam-bath to complete the reaction. The salt of this tertiary amine that results precipitates as a solid mesh of crystals or as a thick gelatinous paste in the case of the higher alkyls. It is dissolved in 12% hydrochloric acid solution, nitrosated at low temperature in the presence of ice with energetic stirring and the secondary amine released by the use of sodium hydroxide and steam distillation in the regular manner as described by Vanino and other laboratory manuals. No attempts were made to separate the nitroso derivative. Yields of these secondary amines ranged from 35 to 73% of the theoretical. The low yields are obtained with the low molecular weight alkyl halides and the higher molecular weight members, hexyl halide and above. To obtain high yields the former should be condensed in a closed vessel to prevent loss through volatilization of the halide, while the high molecular weight members react too slowly to give high yields before appreciable decomposition takes its toll.

The Tertiary Amines.—The dialkyl amino alcohols were made by condensation on the steam-bath of the secondary amine with 20% excess over the equivalent amount of the chlorohydrin. The tertiary base is set free, removed from the water solution by ether extraction, dried by means of anhydrous sodium sulfate and recovered by careful fractional distillation. The use of reduced pressure lessens the decomposition and increases the yields.

TABLE I

BOILING POINTS OF SOME SECONDARY AND TERTIARY AMINES

	B. p., °C.		B. p., °C.
Ethylmethylamine	36–37	γ-Ethylmethylaminopropanol	170
Ethylisopropylamine	76	β-Phenylethylaminoethanol	268
Ethyl-*n*-butylamine	108–9	β-Ethylisopropylaminoethanol	175
Ethylmethylaniline	202	γ-Ethylisopropylaminopropanol	188
Ethylisopropylaniline	211	β-Ethyl-*n*-butylaminoethanol	195
Ethyl-*n*-butylaniline	247		

TABLE II

SOME PROPERTIES OF CERTAIN ALKAMINE ESTERS

	Hydrochlorides	Formula	M. p., °C.	Nitrogen, % Calcd.	Found
A	γ-Ethylmethylaminopropyl benzoate[a]	$C_{13}H_{19}NO_2 \cdot HCl$	123	5.46	5.32
B	β-Phenylethylaminoethyl propionate[b]	$C_{13}H_{19}NO_2 \cdot HCl$	171	5.46	5.56
C	β-Ethylisopropylaminoethyl benzoate	$C_{14}H_{21}NO_2 \cdot HCl$	96	5.15	5.13
D	γ-Ethylisopropylaminopropyl benzoate	$C_{15}H_{23}NO_2 \cdot HCl$	105	4.90	4.87
E	β-Ethyl-*n*-butylaminoethyl cinnamate[5]	$C_{17}H_{25}NO_2 \cdot HCl$	151	4.49	4.42
F	γ-Diethylaminopropyl *p*-methoxycinnamate[c,6]	$C_{17}H_{25}NO_3 \cdot HCl$	142	4.27	4.30
G	γ-Piperidylpropyl *p*-nitrobenzoate[d]	$C_{15}H_{20}N_2O_4 \cdot HCl$	205		
H	γ-Piperidylpropyl *p*-aminobenzoate[e,7]	$C_{15}H_{22}N_2O_2 \cdot HCl$	213	9.38	9.40

[a] Slightly deliquescent. [b] Quite irritating to tongue; acid to litmus. [c] Compound slightly more toxic than apothesin.[7] [d] Free from the hydrochloride, m. p. 78°. [e] Free from the hydrochloride, m. p. 49°.

The compounds A, B, C, D, E, F and H possess anesthetic properties. The irritating effects of (B) are so pronounced that its anesthetic properties

[5] Brill, U. S. Patent, 1,817,670 (1931).

[6] Wildman and Throp, U. S. Patent, 1,193,649 (1916).

[7] Barnes and Adams, THIS JOURNAL, **49**, 1313 (1927).

are not so apparent. The results of careful tests for the physiological properties which are being made on these substances will be reported in a subsequent communication.

Summary

1. Several alkamine alcohols of the type $HO-(CH_2)_nN^x_y$ and secondary and tertiary amines are described.
2. Esters of these alcohols are recorded and described.
3. These esters are reported to possess anesthetic properties.

OXFORD, OHIO

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

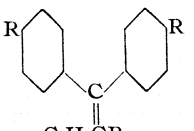
SYNTHESES WITH TRIARYLVINYLMAGNESIUM BROMIDES. TRIARYLACRYLIC ACIDS AND THE INDONES DERIVED FROM THEM

BY C. FREDERICK KOELSCH[1]

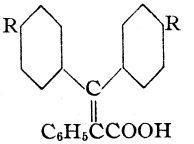
RECEIVED FEBRUARY 6, 1932 PUBLISHED JUNE 6, 1932

It has been shown recently[2] that triphenylvinyl bromide reacts with magnesium to form a Grignard reagent which can be carbonated to give triphenylacrylic acid. The present paper describes the results obtained in similar reactions where certain substituted triphenylvinyl bromides were used

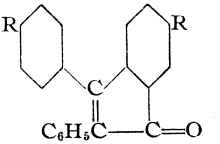
Two disubstituted triphenylvinyl bromides were studied: α-phenyl-β,β-di-*p*-tolylvinyl bromide (I, R = CH_3) and α-phenyl-β,β-di-*p*-anisylvinyl bromide (I, R = OCH_3). Both of these compounds reacted with magnesium to form Grignard reagents which on carbonation yielded the correspondingly substituted acrylic acids (II). The elimination of water from these acids led to the formation of 6-methyl-2-phenyl-3-*p*-tolylindone (III, R = CH_3) and of 3-*p*-anisyl-6-methoxy-2-phenylindone (III, R = OCH_3)



I



II



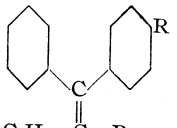
III

While all monosubstituted triphenylvinyl bromides having the substituent in one of the β-phenyl groups should exist in two stereoisomeric forms, the isolation of both of these forms was accomplished in only one of three cases studied. α,β-Diphenyl-β-*p*-chlorophenylvinyl bromide was obtained in the *cis* form (IV, R = Cl) and in the *trans* form (V, R = Cl); only the *cis* form of α,β-diphenyl-β-*p*-tolylvinyl bromide (IV, R = CH_3),

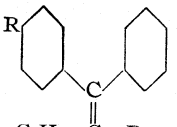
[1] National Research Fellow in Chemistry.

[2] Koelsch, THIS JOURNAL, **54**, 2045 (1932).

and only the *trans* form of α,β-diphenyl-β-*p*-anisylvinyl bromide (V, R = OCH_3) could be isolated.

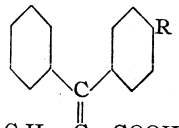


IV

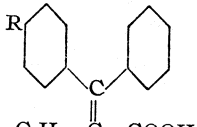


V

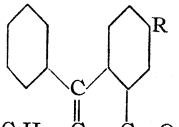
These bromides all reacted readily with magnesium to form Grignard reagents whose subsequent carbonation gave triarylacrylic acids. α,β-Diphenyl-β-*p*-tolylvinylmagnesium bromide gave one acid, *cis*-α,β-diphenyl-β-*p*-tolylacrylic acid (VI, R = CH_3). α,β-Diphenyl-β-*p*-anisylvinylmagnesium bromide gave a mixture of *cis*-α,β-diphenyl-β-*p*-anisylacrylic acid (VI, R = OCH_3) and the corresponding *trans* acid (VII, R = OCH_3) in the ratio of about one part of the *cis* to seven parts of the *trans* compound. The Grignard reagent from *cis*-α,β-diphenyl-β-*p*-chlorophenylvinyl bromide gave a mixture of *cis* and *trans* α,β-diphenyl-β-*p*-chlorophenylacrylic acids in which the *cis* acid (VI, R = Cl) greatly predominated; the Grignard reagent from the isomeric *trans* bromide gave a similar mixture of which *trans*-α,β-diphenyl-β-*p*-chlorophenylacrylic acid (VII, R = Cl) was the more abundant constituent.



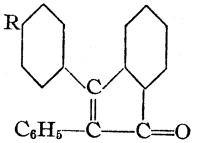
VI



VII



VIII



IX

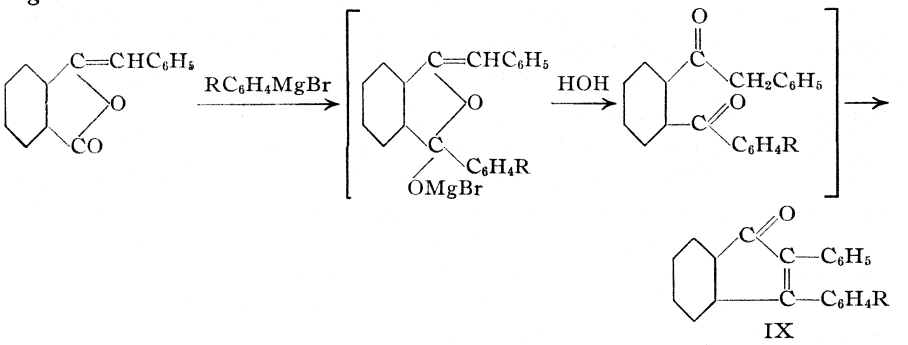
In determining the steric relationship of the phenyl groups in these triarylacrylic acids, *i. e.*, in assigning them to the *cis* or *trans* series, use was made of their ring closure to indones. It is apparent from an inspection of their formulas that a *cis* acid (VI) will give a 6-substituted-2,3-diphenylindone (VIII), while a *trans* acid (VII) will give a 3-*p*-substituted-phenyl-2-phenylindone (IX).

Thionyl chloride in carbon tetrachloride was found to be an ideal reagent for bringing about this ring closure, in that by its use the high temperature (200°) necessary when zinc chloride is employed[3] was avoided. Such a high temperature has been shown to bring about isomerization of

[3] Meyer and Weil, *Ber.*, **30**, 1284 (1897).

certain substituted cinnamic acids.[4] Sulfuric acid, which has been used for the preparation of 2,3-diphenylindone from triphenylacrylic acid,[5] was found to be unusable because of its destructive action toward the methoxylated acids. Under the conditions developed for carrying out the reaction with thionyl chloride, a pure triarylacrylic acid gave practically the theoretical yield of a pure indone, pointing to the absence of rearrangement.

One of each pair of structurally isomeric indones corresponding to one of each pair of stereoisomeric triarylacrylic acids was synthesized according to the reactions[6]



IX

After the structure of one of the isomeric indones had been determined by this synthesis, that of the other was assigned by elimination.

The assignment of *cis* and *trans* structures to the triarylvinyl bromides rests on grounds less secure than those underlying the assignment of these structures to the triarylacrylic acids. To give structures to the bromides, it was necessary to assume that no "inversion" had taken place during two reactions, each of which involved the replacement of an atom or group whose presence was responsible for the isomerism. Such an assumption appears to be little warranted, especially since it is here shown that *some* "inversion" at least occurred in the synthesis of α,β-diphenyl-β-*p*-chlorophenylacrylic acid and of α,β-diphenyl-β-*p*-anisylacrylic acid. In the present paper, the prefixes *cis* and *trans* have been applied to the bromides mainly for convenience in nomenclature.

Experimental

Two methods are available for the preparation of triarylvinyl bromides

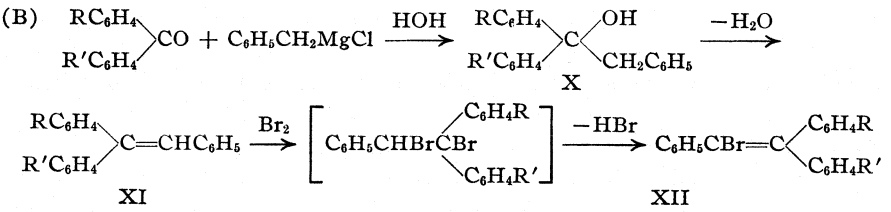
$$\text{(A)}\quad C_6H_5CH_2COOEt + 2p\text{-}RC_6H_4MgBr \xrightarrow{HOH} \underset{X}{C_6H_5CH_2C(OH)(C_6H_4R)_2} \xrightarrow{-H_2O}$$

$$\underset{XI}{C_6H_5CH{=}C(C_6H_4R)_2} \xrightarrow{Br_2} [C_6H_5CHBrCBr(C_6H_4R)_2] \xrightarrow{-HBr} C_6H_5CBr{=}C(C_6H_4R)_2$$

[4] Stoermer and Voht, *Ann.*, **409**, 40, 53 (1915).

[5] Weitz and Scheffer, *Ber.*, **54**, 2341 (1921).

[6] Löwenbein and Ulich, *ibid.*, **58**, 2662 (1925); Weiss and Sauermann, *ibid.*, p. 2736.



While method (A) is applicable to the synthesis of only disubstituted compounds and was used to prepare only α-phenyl-β,β-di-*p*-anisylvinyl bromide, method (B) is of general application and was used for the preparation of the other bromides described in this paper (XII, R = R′ = CH_3; or R′ = H and R = CH_3, OCH_3, or Cl). The yields in all reactions involved in either method were usually over 90%.

The Carbinols (X). Table I.—In order to isolate the carbinols, it was necessary to decompose the intermediate ROMgX compounds with ammonium chloride solution and to exclude mineral acids, which readily effect the elimination of water. The carbinols may be converted directly into the bromides by treating their 30% solutions in acetic acid with a slight excess of a 40–50% solution of bromine in acetic acid. They were recrystallized from ethanol containing a little ammonia.

TABLE I

THE CARBINOLS

( )-ethanol	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
α,α-Di-*p*-tolyl-β-phenyl-	(Not isolated)					
α,α-Di-*p*-anisyl-β-phenyl-	140	$C_{22}H_{22}O_3$	[a]			
α,β-Diphenyl-α-*p*-tolyl-	89	$C_{21}H_{20}O$	87.5	6.94	87.3	6.5
α-*p*-Anisyl-α,β-diphenyl-	112	$C_{21}H_{20}O_2$	[b]			
α-*p*-Chlorophenyl-α,β-diphenyl-	83	$C_{20}H_{17}OCl$	77.7	5.51	77.7	5.61

[a] Roca, *Anales soc. españ. fís. quím.*, **15**, 29 (1917); *Chem. Abstracts*, **12**, 475 (1918).
[b] Ley and Kirchner, *Z. anorg. allgem. Chem.*, **173**, 395 (1928).

The Ethylenes (XI). Table II.—The ethylenes were prepared by distilling the carbinols under reduced pressure in the presence of a trace of sulfuric acid.

TABLE II

THE ETHYLENES

( )-ethylene	B. p., °C. (mm.)	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
					91.5	7.1
α,α-Di-*p*-tolyl-β-phenyl-	258–259 (24)	$C_{22}H_{20}$	92.9	7.1	91.4	7.0
α,α-Di-*p*-anisyl-β-phenyl-	283–285 (18)	$C_{22}H_{20}O_2$	(Ref. *a*, Table I)			
α,β-Diphenyl-α-*p*-tolyl-	245–250 (27)	$C_{21}H_{18}$	93.2	6.7	93.2	6.5
α-*p*-Anisyl-α,β-diphenyl-	260–270 (25)	$C_{21}H_{18}O$	(Ref. *b*, Table I)			
α-*p*-Chlorophenyl-α,β-diphenyl-	(Not isolated)					

The Triarylvinyl Bromides (XII). Table III.—Bromination of the carbinols or of the ethylenes in acetic acid according to the procedure which has been described for the preparation of triphenylvinyl bromide[2] gave the substituted triphenylvinyl bromides. In general, they were purified by crystallization from alcohol.

TABLE III

THE BROMIDES

( )-vinyl bromide	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
β,β-Di-*p*-tolyl-α-phenyl-	132–133	$C_{22}H_{19}Br$	72.7	5.23	72.8	5.19
β,β-Di-*p*-anisyl-α-phenyl-	109–111	$C_{22}H_{19}O_2Br$	66.8	4.82	66.7	4.82
α,β-Diphenyl-β-*p*-tolyl-	114–116	$C_{21}H_{17}Br$	72.2	4.87	72.2	4.76
β-*p*-Anisyl-α,β-diphenyl-	118–120	$C_{21}H_{17}OBr$	69.1	4.66	68.8	4.66
cis-β-*p*-Chlorophenyl-α,β-diphenyl-	156–158	$C_{20}H_{14}ClBr$	65.0	3.79	65.0	4.2
trans-β-*p*-Chlorophenyl-α,β-diphenyl-	103–105	$C_{20}H_{14}ClBr$	65.0	3.79	64.6	3.54

Extended fractional crystallization of α,β-diphenyl-β-*p*-anisylvinyl bromide and of α,β-diphenyl-β-*p*-tolylvinyl bromide from benzene, carbon tetrachloride or acetic acid did not effect a separation of either compound into two forms. In both cases a small amount of low melting substance was obtained from the first mother liquors, but no pure substance could be isolated from this.

Separation of α,β-Diphenyl-β-*p*-chlorophenylvinyl Bromide into *Cis* and *Trans* Forms.—Water was added to the acetic acid solution in which the bromide had been prepared and the crude bromide thus obtained, which slowly solidified, was crystallized from ethanol, in which it is quite difficultly soluble, to remove a small amount of oily impurities. The crystalline mixture (60 g.) was dissolved in 50 ml. of hot benzene, and 50 ml. of methanol was added. On cooling the solution, 27 g. of bromide melting at 155–157° crystallized. This, redissolved in 30 ml. of hot benzene and reprecipitated by the addition of 30 ml. of methanol, gave 25 g. of pure *cis* bromide, m. p. 156–158°. The oily residue left after the removal of the solvents from the combined mother liquors by distillation under reduced pressure was dissolved in 200 ml. of hot ethanol. Cooling this solution gave 27.5 g. of practically pure *trans* bromide, m. p. 100–105°.

Carbonation of the Triarylvinylmagnesium Bromides. The Triarylacrylic Acids. Table IV.—The Grignard reagents were prepared from 10 g. of a bromide, 0.05 ml. of ethyl bromide, a small crystal of iodine, 1.1 equivalents of magnesium and 100 ml. of ether.

The Grignard reagents were carbonated by leading in dry carbon dioxide as long as it was absorbed. Decomposition of the magnesium compounds with dilute sulfuric acid and extraction of the resulting ethereal solutions with dilute sodium carbonate gave aqueous solutions of the sodium salts

of the triarylacrylic acids. From these the organic acids were precipitated with dilute hydrochloric acid. They were recrystallized from acetic acid.

TABLE IV

THE ACIDS

No.	( )-acrylic acid	M. p., °C.	Color with concd. H_2SO_4 Cold	Hot
1	α-Phenyl-β,β-di-*p*-tolyl-	205–206	Brown-yellow	Scarlet
2	α-Phenyl-β,β-di-*p*-anisyl-	169–170	Red-violet	Orange-red
3	*cis*-α,β-Diphenyl-β-*p*-tolyl-	185–195	Emerald green	Dark red
4	*cis*-α,β-Diphenyl-β-*p*-anisyl-	179–180	Brown-orange	Red
5	*trans*-α,β-Diphenyl-β-*p*-anisyl-	153–155	Brown-orange	Red
6	*cis*-α,β-Diphenyl-β-*p*-chlorophenyl-	203–205	Emerald green	Red-violet
7	*trans*-α,β-Diphenyl-β-*p*-chlorophenyl-	205–211	Emerald green	Red-violet

No.	Formula	Neut. equiv. Calcd.	Found	Analyses Calcd. C	H	Found C	H
1	$C_{23}H_{20}O_2$	328	327	84.0	6.1	84.2	6.05
2	$C_{23}H_{20}O_4$	360	354	76.6	5.56	76.5	5.67
3	$C_{22}H_{18}O_2$	314	308	84.0	5.73	83.2	5.77
4	$C_{22}H_{18}O_3$	330	333	80.0	5.45	80.0	5.6
5	$C_{22}H_{18}O_3 + {}^1/_2H_2O$	339	338	77.8	5.6	77.5, 77.4	5.4, 5.6
6	$C_{21}H_{15}O_2Cl$	335	328	75.2	4.48	75.6	4.45
7	$C_{21}H_{15}O_2Cl$	335	324	75.2	4.48	75.4	4.48

Separation of α,β-Diphenyl-β-*p*-anisylacrylic Acid into *Cis* and *Trans* Forms.—Fractional solution in ether followed by crystallization from acetic acid gave the two forms of this acid. The higher melting *cis* acid is nearly insoluble in ether, while the *trans* acid is readily soluble.

α,β-Diphenyl-β-*p*-chlorophenylacrylic Acids.—The mixture of *cis* and *trans* acids obtained from 10 g. of the pure *cis* (or *trans*) bromide was separated by repeated fractional crystallization from carbon tetrachloride into 3–3.5 g. of *cis* (or *trans*) acid and an approximately equal weight of a mixture of *cis* and *trans* acids (neut. equiv., calcd.: 335; found: 327) which melted at 178–195° and which gave a separable mixture of isomeric chlorodiphenylindones on treatment with thionyl chloride.

α,β-Diphenyl-β-*p*-tolylacrylic Acid.—Despite the unsharp melting point of this acid, the presence of isomers in it could not be demonstrated by repeated fractional crystallizations. Furthermore, the indone obtained from it was homogeneous.

The Indones. Table V.—To a solution of 0.5 g. of a triarylacrylic acid in 2 ml. of dry carbon tetrachloride was added 0.5 ml. of thionyl chloride. The solution was refluxed for four hours, cooled and poured into water. The carbon tetrachloride was expelled by boiling, leaving the indone crystalline and melting only a few degrees lower than the pure compound. Recrystallization from acetic acid gave the pure ketone in a yield of 0.35–0.45 g.

TABLE V

THE INDONES

No.	( )-indone	M. p., °C.	Form	Color[a]
1	2-Phenyl-3-*p*-anisyl-6-methoxy-	153–154	Needles	Dark red
2	2-Phenyl-3-*p*-tolyl-6-methyl-	161–161.5	Needles	Bright red
3	2,3-Diphenyl-6-methyl-	175–177	Flat needles	Bright red
4	2-Phenyl-3-*p*-tolyl-[b]	133–134	Prisms	Maroon
5	2,3-Diphenyl-6-methoxy-	167–168	Prisms	Garnet red
6	2-Phenyl-3-*p*-anisyl-[c]	114–115	Needles	Scarlet
7	2,3-Diphenyl-6-chloro-	186–188	Plates	Orange
8	2-Phenyl-3-*p*-chlorophenyl-[c]	162–164	Prisms	Orange

[a] The indones give color reactions with sulfuric acid identical with those given by the acrylic acids from which they are prepared. [b] Obtained from benzalphthalide. [c] Same compound obtained from benzalphthalide and from the appropriate acrylic acid.

		Analyses			
		Calcd.		Found	
No.	Formula	C	H	C	H
1	$C_{23}H_{18}O_3$	80.6	5.26	80.6	5.39
2	$C_{23}H_{18}O$	89.0	5.8	89.2	5.65
3	$C_{22}H_{16}O$	89.1	5.4	89.0	5.56
4	$C_{22}H_{16}O$	89.1	5.4	88.5	5.32
5	$C_{22}H_{16}O_2$	84.5	5.13	84.4	5.45
6	$C_{22}H_{16}O_2$	84.5	5.13	84.4	4.98
7	$C_{21}H_{13}OCl$	79.5	4.11	79.6	4.22
8	$C_{21}H_{13}OCl$	79.5	4.11	79.2	4.28

The preparation of 2-phenyl-3-*p*-substituted-phenylindones from benzalphthalide was carried out according to the procedure described in the literature.[6] Mixed melting points proved the identity of the compounds thus prepared with the appropriate ones obtained from the triarylacrylic acids.

Summary

It has been shown that the formation of Grignard reagents from triarylvinyl bromides is a quite general reaction.

A number of triarylacrylic acids have been prepared from triarylvinylmagnesium bromides, and in the cases where these acids exist in stereoisomeric forms it has been possible to assign structures to the isomers isolated.

The triarylacrylic acids have been found to undergo ring closure to form indones when they are treated with thionyl chloride.

CAMBRIDGE, MASSACHUSETTS

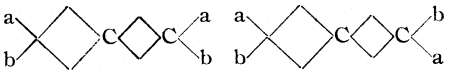
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STEREOCHEMISTRY OF CARBODIIMIDES. XXII[1,2]

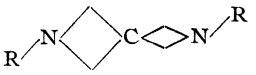
BY L. J. ROLL AND ROGER ADAMS

RECEIVED FEBRUARY 6, 1932 PUBLISHED JUNE 6, 1932

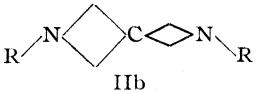
The preparation of stereoisomeric allenes of Type I (a and b) has been the subject of many investigations from the time van't Hoff first predicted that such compounds should be capable of existing in optically active forms. Somewhat analogous to the allenes is another class of asymmetric molecules, the carbodiimides II (a and b).



I (a and b)



IIa



IIb

On the assumption that the nitrogen atom has a fixed tetrahedral structure, it may be seen that the two substituting R groups are in planes different from those of the C=N linkages and, therefore, a pair of mirror images may exist even though the two R groups in the molecule are the same. If, on the other hand, the R groups may vibrate through the axis common to the N=C=N nucleus, isomerism will disappear whether the R groups are the same or different.

The results of many researches have indicated that trivalent nitrogen compounds of the type RR'R"N can be obtained optically active only with great difficulty or not at all. In fact, as yet no optically active trivalent nitrogen compounds have been isolated and as a consequence it has been assumed that the nitrogen atom in such molecules is probably very mobile and that the three valence bonds and the pair of unshared electrons may vibrate through such positions that optical isomerism will be prevented. On the other hand, *cis–trans* isomerism in the oximes is commonly explained on the assumption of a fixed tetrahedral nitrogen atom. It would follow, therefore, that the lack of mobility of the groups on the nitrogen atom in these molecules is due, presumably, to the presence of C=N. Since double bonds exist in carbodiimides, optical isomerism may be anticipated in this class of compounds.[3]

[1] For previous paper see White and Adams, THIS JOURNAL, **54**, 2104 (1932).

[2] This communication is an abstract of a portion of a thesis submitted by L. J. Roll in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Faltis, Pirsch and Bermann, *Ber.*, **63**, 691 (1931), were unable to obtain stereoisomers of certain allene derivatives and have suggested a different conception of allene linkages which would involve no optical isomerism. Such an argument, though not too convincing, might also be applied to carbodiimides.

In this preliminary investigation an attempt has been made to obtain optically active carbodiimides. The results thus far have been unsuccessful, due to certain inherent properties of these compounds which have introduced difficulties not as yet overcome. Carbodiimides are not only very reactive to reagents such as water, acids, etc., but they polymerize readily merely on standing at room temperature. The possibility of studying an amino or carboxy substituted diphenylcarbodiimide which might be resolved in the usual way was soon eliminated since the carboxy and amino derivatives of diphenyl carbodiimide could not be prepared by the ordinary methods. Even if such compounds could be synthesized, the probability of the formation of the salts and subsequent resolution without decomposition seemed remote. A much more feasible line of attack appeared to be the preparation of a mono- or dicarbo-*l*-menthoxythiocarbanilide which, upon elimination of hydrogen sulfide, should yield a mixture of separable diastereoisomeric carbodiimides. Unfortunately, the resulting reaction mixture after such treatment of monocarbo-*l*-menthoxy carbanilide was an oil which did not solidify but which polymerized gradually on standing. From this experiment it is obvious that the carbodiimide synthesized for the purpose proposed must be of such a character that the monomer is a solid which can be separated and kept in the solid form so as to prevent or greatly diminish the rate of polymerization.

The dicarboethoxy and the monocarboethoxy diphenylcarbodiimides were also oils and the dibromo derivative which has been reported previously in the literature would not solidify at room temperature.

A considerable portion of the time of this preliminary investigation was devoted to the general study of carbodiimides. Without attempting to review in detail the previous literature,[4] it may be pointed out that diphenylcarbodiimide is an unstable liquid which polymerizes with ease. There appears to be an authentic crystalline tripolymer and a higher amorphous polymer. That two dimers exist also seems probable.

More recently Herzog[5] has patented what he calls diphenylcarbodiimide resins. He reports a number of reagents for eliminating hydrogen sulfide from thiocarbanilides in order to obtain the carbodiimide from which the polymer may be produced. It is questionable, however, whether Herzog ever obtained resinous carbodiimides.

[4] Weith, *Ber.*, **7**, 10, 1305 (1874); Laubenheimer, *ibid.*, **13**, 2155 (1880); Schall and Paschkowetzky, *ibid.*, **25**, 2880 (1892); Schall, *ibid.*, **26**, 3064 (1893); **27**, 2260 (1894); McCoy, *ibid.*, **30**, 1090 (1897); Busch, Blum and Pings, *J. prakt. Chem.*, **79**, 11, 513 (1909); Schall, *ibid.*, **81**, 11, 191 (1910); Miller and Plöchl, *Ber.*, **27**, 1283 (1894); **28**, 1004 (1895); Schall, *J. prakt. Chem.*, **53**, 11, 139 (1896); *Ber.*, **27**, 2696 (1894); Short and Smith, *J. Chem. Soc.*, **121**, 1803 (1922).

[5] Herzog, *Z. angew. Chem.*, **33**, 140 (1920); see also Merz, Weith, *Chem. Zentr.*, **40**, 977, 993 (1869); Hoffmann, *Ann.*, **70**, 148 (1849); Ellis, "Synthetic Resins and Their Plastics," The Chemical Catalog Company, New York, 1923, p. 245.

In this investigation a careful study of the conversion of thiocarbanilide into carbodiimide has indicated that if the temperature during the reaction is much above 80°, not only is diphenylcarbodiimide produced, but simultaneously the thiocarbanilide is broken up into aniline and phenylisothiocyanate. Aniline then immediately reacts with the diphenylcarbodiimide with the formation of triphenylguanidine, which is the main product of the reaction.

$$C_6H_5NHCSNHC_6H_5 \longrightarrow C_6H_5N{=}C{=}NC_6H_5 + H_2S$$

$$C_6H_5N{=}C{=}S + NH_2C_6H_5$$

$$C_6H_5N{=}C{=}NC_6H_5 + NH_2C_6H_5 \longrightarrow C_6H_5N{=}C(NHC_6H_5)(NHC_6H_5)$$

Herzog claims to have obtained polymeric diphenyl carbodiimide by heating thiocarbanilide with aniline in the presence of arsenious oxide. Upon repetition of his experiment, however, an excellent yield of triphenylguanidine was produced. Moreover, substitution of the arsenious oxide by cadmium carbonate or mercuric oxide gave consistently the same result. It was noticed, also, that if triphenylguanidine was heated somewhat above its melting point and allowed to cool, a brittle, transparent resin was produced which leaves a hard, transparent film on evaporation of a solution in the usual lacquer solvents. This resin was essentially monomeric in character as shown by molecular weight determinations.

At 80° the only satisfactory reagent for conversion of the thiocarbanilides was mercuric oxide. Under these conditions an excellent yield of monomeric diphenylcarbodiimide was produced which, however, gradually polymerized upon standing. A number of new substituted thiocarbanilides were made but it was found that the elimination of hydrogen sulfide takes place only with great difficulty when certain types of substituents are present. This fact has greatly limited the number of substituted diphenylcarbodiimides which could be prepared and studied.

Experimental

Elimination of Hydrogen Sulfide from Thiocarbanilide with Various Reagents. Triphenylguanidine.—A mixture of 22.8 g. (1 mole) of thiocarbanilide, 13.2 g. of arsenic trioxide (6 moles) and 11 g. (2 moles) of calcium oxide was placed in a 500-cc. flask fitted with a stirrer, thermometer and a reflux condenser. To this was added 75 cc. of dry xylene, then the stirrer was started and heat applied. The reaction mixture was held at 145° for fourteen hours and then filtered hot. From the filtrate a white solid separated. The triphenylguanidine was purified by recrystallization from benzene and then melted at 142–143°. The yield was 10 g. (70%).

By using cadmium carbonate in place of arsenic trioxide, a 48% yield of triphenylguanidine resulted, and with yellow mercuric oxide a 35% yield.

Elimination of Hydrogen Sulfide from Thiocarbanilide. Diphenylcarbodiimide.—By following exactly the procedure just described using yellow mercuric oxide except that benzene was substituted for xylene and the reaction was run at 80° instead of 145°,

diphenylcarbodiimide was produced which boiled at 142° at 5 mm. From 22.8 g. of thiocarbanilide, 8.5 g. of product was obtained. After five or six days the liquid carbodiimide had completely solidified to a product melting at 158–160°. Molecular weight determination indicated the liquid to be monomolecular.

No elimination of hydrogen sulfide took place at 80° when arsenic trioxide was used in place of the mercuric oxide.

Formation of a Resin-like Substance from Triphenylguanidine.—Two grams of triphenylguanidine was heated in a small crucible at 180° for two hours. Upon cooling, an amber-colored, brittle, glass-like solid which melted at 129–137° resulted. The molecular weight of this product by freezing point in benzene showed it to be 318 as compared with a theoretical of 287 for triphenylguanidine.

This resin, when dissolved in a mixture of benzene, butyl alcohol and ethyl acetate and poured on to a glass surface, yielded a transparent, hard film upon evaporation of the solvent.

***p*-Carbo-*l*-menthoxythiocarbanilide.**—A solution of 6.75 g. of phenyl isothiocyanate and 13.75 g. of menthyl *p*-aminobenzoate in 50 cc. of benzene was refluxed on a steam-bath for twenty hours. Two-thirds of the solvent was then distilled and the product allowed to crystallize. It was purified by crystallizing first from a mixture of benzene and 60–70° petroleum ether, and then from benzene and finally from alcohol. The yield was 15 g. of a product melting at 124–125°.

Anal. Calcd. for $C_{23}H_{30}O_2N_2S$: N, 6.83. Found: N, 7.43.

***p*-Carbo-*l*-menthoxydiphenylcarbodiimide.**—Sixteen grams of *p*-carbo-*l*-menthoxydiphenylthiourea, 16 g. of yellow mercuric oxide and 10 g. of powdered anhydrous calcium chloride were mixed with 100 cc. of dry benzene and refluxed with stirring for five hours. The cold mixture was filtered and the filtrate warmed on the steam-bath until the solvent was removed. A dark viscous oil was obtained which solidified upon standing overnight to an amorphous mass, insoluble in benzene.

***p,p'*-Dicarboethoxydiphenylcarbodiimide.**—From 22 g. of the *p,p'*-dicarboethoxydiphenylthiourea,[6] following the same procedure for the preparation of *p*-carbo-*l*-menthoxydiphenylcarbodiimide, there was obtained 17 g. of an amber-colored viscous liquid which on standing at room temperature for about thirty days gradually solidified to a transparent, amber-like solid melting at 78–90°.

Anal. Calcd. for $C_{19}H_{18}O_4N_2$: N, 8.28. Found: N, 8.48.

Symmetrical Tri-(*p*-carboethoxy-phenyl)-guanidine.—A mixture of 11 g. of *p,p'*-dicarboethoxydiphenylthiourea, 13 g. of yellow mercuric oxide and 4 g. of powdered calcium oxide was placed in a 500-cc. flask fitted with a thermometer, mechanical stirrer and reflux condenser. Seventy-five cc. of dry xylene was added, heat applied and the reaction mixture stirred. After four hours at 135°, the solution was filtered while hot and the filtrate concentrated to 20 cc. The white precipitate which formed upon cooling was crystallized from a mixture of pyridine and petroleum ether. The product melted at 170–171°. The yield was 4 g.

Anal. Calcd. for $C_{25}H_{23}N_3O_6$: C, 65.73; H, 4.99. Found: C, 65.01; H, 5.18.

***p,p'*-Dibromodiphenylcarbodiimide.**[7]—The *p,p'*-dibromodiphenylthiourea was made according to the procedure of Fry and treated according to the previously described procedure with mercuric oxide and calcium chloride in dry benzene. A dark, viscous residue was obtained which distilled under diminished pressure at 208–212° at 4 mm. Upon standing, this viscous distillate gradually solidified to a resin-like solid.

[6] Fry, THIS JOURNAL, **35**, 1539 (1913).

[7] Ingold, *J. Chem. Soc.*, **125**, 101 (1924).

Summary

1. The structural relationship of allenes and diaryl carbodiimides has been pointed out and a method for proving the asymmetry of the carbodiimide proposed.

2. Experiments on the preparation of various carbodiimides have been described and the difficulties in the study of these substances pointed out.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY AND THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

INVESTIGATIONS ON THE STEREOISOMERISM OF UNSATURATED COMPOUNDS. I. THE COMPOSITION OF CROTONALDEHYDE

BY WILLIAM G. YOUNG[1]

RECEIVED FEBRUARY 8, 1932 PUBLISHED JUNE 6, 1932

The program of research undertaken includes a study of the physical and chemical properties of a series of aliphatic hydrocarbons containing conjugated systems of double bonds. Since these compounds may occur in several stereoisomeric forms, it is necessary to isolate the individual isomers in order to obtain reliable physico-chemical measurements. Such procedure will enable one to determine the influence of the configuration of the individual double bonds on the physical and chemical properties of these hydrocarbons.

The keynote in this work is purity of materials. For this reason the separation of isomeric mixtures by fractional distillation was avoided because of the inherent difficulties.[2] Instead of this, the author is studying methods of synthesis which will lead to the production of pure isomers, the first of which is *trans,trans,trans*-dimethylhexatriene. To do this, one must know the configuration of the starting materials as well as the intermediate compounds.

One of the starting materials investigated is the so-called crotonaldehyde which is commonly obtained from aldol. This material might be a mixture of *cis*- and *trans*-crotonaldehydes and vinyl acetaldehyde. If this is the case the resulting hexatriene might be a mixture of as many as eight different isomeric hydrocarbons. Therefore a quantitative study of ordinary crotonaldehyde[3] was undertaken by several different methods. The first re-

[1] The experimental part of this work was completed while the author was a National Research Fellow in Chemistry at Stanford University. This paper was presented at the Pasadena meeting of the American Association for the Advancement of Science, June 19, 1931. Original manuscript received June 29, 1931.

[2] Lucas, Dillon and Young, THIS JOURNAL, **52**, 1949 (1930).

[3] Commercial crotonaldehyde was obtained from one manufacturer in order to ensure an unlimited supply of material of constant composition.

sults are presented in this article, namely, oxidation with oxygen and with silver oxide.

Previous Investigations on the Composition of Crotonaldehyde by Oxidation.—Several investigators[4] have reported the oxidation of crotonaldehyde preparations but the composition of none of these has been conclusively established. Kekulé[4a] and Charon[4b] obtained *trans*-crotonic acid by oxidation with air or oxygen and concluded that their material was *trans*-crotonaldehyde. Duchesne and Délépine[4c] recovered in addition some acetic acid and Kaufler,[4f] using a more elaborate method, isolated still another product, *cis*-crotonic acid in 6% yields. Unfortunately neither the source of the aldehyde nor the method of oxidation was adequately described by Kaufler.

Kekulé,[4a] Charon[4b] and Délépine and Bonnet[4d] used silver oxide in the oxidation of crotonaldehyde. Of these, only Charon carefully avoided stereomutation of the materials, and indicated that his product was pure *trans*-crotonic acid. Inasmuch as he extracted this product from the acidified reaction mixture with ether, it is quite possible that appreciable quantities of the extremely soluble *cis*-crotonic acid may have been lost in the mother liquor. In view of the uncertainty of this question we have attempted to ascertain whether or not *cis*-crotonic acid is actually a product of the oxidation of crotonaldehyde.

Any chemical reactions to which crotonaldehyde is submitted must be performed under carefully controlled conditions in order to avoid stereomutation either in the aldehyde or in its reaction products. Stereomutation of *cis* isomers readily occurs in the case of *cis*-crotonic acid and its homologs,[5,6] especially if traces of catalysts are present, and equilibria involving stereomutation of *trans* isomers have been observed at temperatures as low as 100°.[7,8] Another possible rearrangement, shifting of the double bond from the α,β to the less stable β,γ position is very unlikely, since there is no substitution in the γ position.[9]

Method of this Investigation.—In the oxidation of crotonaldehyde the experiments were designed to account quantitatively for all of the crotonic acids formed during the oxidation and to avoid conditions favoring molecular rearrangements during the oxidation process and subsequent treatment.

For comparison two series of experiments were run: one on the commer-

[4] (a) Kekulé, *Ann.*, **162,** 100 (1872); (b) Charon, *Ann. chim. phys.*, [7] **17,** 216 (1897); (c) Délépine, *ibid.*, [8] **16,** 136 (1909); (d) Délépine and Bonnet, *Compt. rend.*, **149,** 40 (1909); *Bull. soc. chim.*, [4] **5,** 882 (1909); (e) Duchesne and Délépine, *ibid.*, [4] **35,** 1311 (1924); (f) Kaufler, *Monatsh.*, **53–54,** 119 (1929).

[5] Wislicenus, *Ann.*, **248,** 341 (1888); *Chem. Zentr.*, II, 259 (1897).

[6] Blaise, *Ann. chim. phys.*, [8] **11,** 116 (1907).

[7] Morrel and Hanson, *J. Chem. Soc.*, **85,** 1520 (1904).

[8] Skau and Saxton, THIS JOURNAL, **52,** 335 (1930).

[9] "Annual Reports on the Progress of Chemistry," **24,** 111 (1927).

cial crotonaldehyde, the other, on *trans*-crotonaldehyde. The *trans*-crotonaldehyde was prepared by treating the original aldehyde with hydrogen chloride and strong sunlight for several hours to transform any possible *cis* isomer which may have been originally present. It is well known that hydrochloric acid catalyzes this change in closely related substances.[5,6]

The original and sunlight-irradiated aldehydes were separately oxidized by two different reagents, gaseous oxygen and alkaline silver oxide. The content of *cis*- and *trans*-crotonic acids in the oxidation mixtures from both series of experiments was estimated by fractional crystallization of their sodium salts.[10] The different salt fractions were analyzed for total crotonate content by titration with bromine water. Although Buckwalter and Wagner[11] reported that crotonic acid is not brominated readily, we have found that the sodium salt is rapidly and quantitatively brominated in neutral solution.

Discussion of Results.—There was excellent agreement between the results on the commercial and sunlight-irradiated aldehydes with both oxygen and silver oxide. No *cis*-crotonic acid was isolated in any of the controlled experiments, though as much as 5% was isolated from the gaseous oxidation of both aldehydes when the temperature of the reaction mixture was *not controlled*. It was therefore concluded that the aldehyde under investigation was free from the *cis* isomer and that *cis*-crotonic acid is not produced during the oxidation of crotonaldehyde under *controlled* conditions. It is indeed unfortunate that Kaufler[4f] did not discuss his method of oxidation, since this part of the work requires the most careful regulation. His *cis*-crotonic acid may readily be accounted for if the reaction temperature were not controlled.

Experimental Procedure

Purification of Crotonaldehyde.—The commercial crotonaldehyde obtained from the Niacet Chemical Corporation was purified by two distillations through an 80-centimeter Vigreux column: b. p. of distillate, 101.3–102.0°; n_D^{20} 1.4356.

Preparation of Trans-Crotonaldehyde.—Commercial crotonaldehyde was placed in a quartz flask with a few cubic centimeters of concentrated hydrochloric acid and exposed to strong sunlight for several hours to remove any *cis*-crotonaldehyde originally present. The reaction mixture was then twice distilled through an 80-cm. Vigreux column: b. p. 101.3–101.7; n_D^{20} 1.4362.

The Oxidation of Crotonaldehyde with Gaseous Oxygen.—The gaseous oxidations of crotonaldehyde were carried out by shaking the material in a closed system in order to follow the oxygen absorption quantitatively. The temperature of the reaction mixture was kept below 30°, since in preliminary experiments the reaction temperature often reached 50–90° in ten or fifteen minutes, accompanied by the formation of some *cis*-crotonic acid and large quantities of resin. When oxygen was no longer absorbed the unchanged crotonaldehyde was distilled from the reaction mixture at 70-mm. pressure

[10] This method of analysis has been used by Wislicenus[5]; Kaufler[4f]; Auwers and Wissebach, *Ber.*, **56**, 715 (1923); and Braun, THIS JOURNAL, **51**, 228 (1929).

[11] Buckwalter and Wagner, *ibid.*, **52**, 5248 (1930).

and again shaken in the absorption apparatus. The products from both oxidations were then combined and separated into four fractions; fraction 1 (b. p. (18 mm.) 31–45°), acetic acid; fraction 2 (b. p. (15 mm.) 45–83°); fraction 3 (b. p. (15 mm.) 83–87°); and an acid-resin residue. The boiling point rose from 45 to 83° in less than thirty seconds and only a few drops of liquid distilled. This indicated the absence of *cis*-crotonic acid and vinylacetic acid. As a further proof for the absence of these substances the crotonic acid, fraction 3, was converted into its sodium salt by neutralization with sodium ethylate and analyzed according to Kaufler.[4f] If the temperature of the reaction mixture was not controlled during the oxidation process, both fraction 2 and fraction 3 contained detectable quantities of *cis*-crotonic acid. Typical results of the experiments with gaseous oxygen are shown in Table I.

The Oxidation of Crotonaldehyde with Silver Oxide.—To make sure that the gaseous method gave dependable results, an entirely different process was resorted to, namely, oxidation with silver oxide. This reagent was more satisfactory than oxygen since the reaction products were free from resin acids and could be readily isolated without danger of rearrangements.[4b] The reaction was performed as follows.

The aldehyde was shaken vigorously with a water suspension of silver oxide at 15–20°. The reaction was complete in six hours. Through metathesis, the silver salt was converted into the sodium salt by shaking with sodium carbonate or sodium hydroxide. The solution was filtered and the filtrate neutralized with 6 *N* sulfuric acid. After the crotonate content of the solution had been determined, the water was removed at 27° under reduced pressure. The residue was then analyzed for *cis*- and *trans*-crotonic acids by Kaufler's method.[4f] All of the crotonate in the solution was thus accounted for as the *trans* isomer. Typical experiments on the original and irradiated aldehydes

TABLE I

THE FRACTIONAL EXTRACTION OF SODIUM CROTONATE RESIDUE OBTAINED FROM THE OXIDATION OF CROTONALDEHYDE

Expt. 1. Original Aldehyde + Oxygen
Expt. 2. Irradiated Aldehyde + Oxygen
Expt. 3. Original Aldehyde + Silver Oxide
Expt. 4. Irradiated Aldehyde + Silver Oxide
Expt. 5. Irradiated Aldehyde + Oxygen (temperature uncontrolled)

EXPERIMENT 1

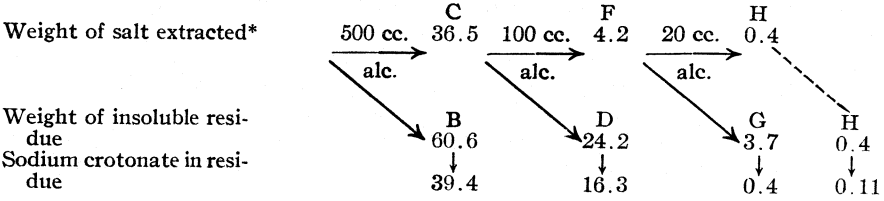
	1st Extn.		2d Extn.		3d Extn.	
	A	C	F		H	
Weight of salt extracted	56.4	3.2	1.7		1.0	
	700 cc. alc. →		100 cc. alc. →		20 cc. alc. →	
	B		D		G	H
Weight of insoluble residue		52.9	1.6		0.7	1.0
Sodium crotonate in residue		52.9	1.6		0.6	0.0

EXPERIMENT 2

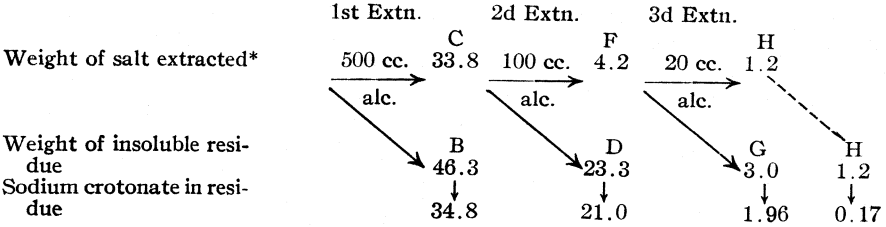
	1st Extn.		2d Extn.		3d Extn.	
	A	C	F		H	
Weight of salt extracted	52.5	3.3	1.6		0.8	
	700 cc. alc. →		100 cc. alc. →		20 cc. alc. →	
	B		D		G	H
Weight of insoluble residue		48.9	1.7		0.8	0.8
Sodium crotonate in residue		48.9	1.55		0.6	0.0

TABLE I (*Concluded*)

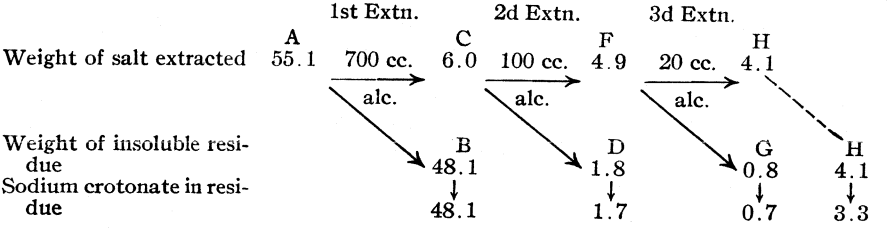
EXPERIMENT 3



EXPERIMENT 4



EXPERIMENT 5



A is the weight of salt at the start of extraction process.

C, F, H are weights of salt dissolved in extractions 1, 2 and 3, respectively.

B, D, G are weights of salt undissolved in extractions 1, 2, 3, respectively.

* The weight of the crude salt was not determined in this case.

are listed in Table I. In all experiments the *cis*-sodium crotonate should be found in the last extract H. From the table it is seen that of the salt dissolved a negligible quantity reacts with bromine, except in experiment 5 where the reaction temperature was not controlled. Therefore if any *cis*-crotonic acid is formed on oxidation with silver oxide or oxygen it is formed in very small amount.

In conclusion the writer desires to express his appreciation of the kindly interest shown by members of the Chemistry Staff at Stanford University and at the Division of Plant Biology of the Carnegie Institution of Washington, located at Stanford, especially to Doctors H. A. Spoehr and J. H. C. Smith, who offered many helpful suggestions and criticisms.

Summary

The composition of crotonaldehyde has been investigated by oxidation with gaseous oxygen and alkaline silver oxide under conditions designed to

avoid molecular rearrangements. It was shown that "niacet" crotonaldehyde is the *trans* isomer by comparison with *trans*-crotonaldehyde prepared by treatment with hydrogen chloride and sunlight. Both aldehydes gave only *trans*-crotonic acid on oxidation under controlled conditions, but some *cis*-crotonic acid when the temperature was not controlled.

It was concluded that the *cis*-crotonic acid reported by Kaufler[4f] was probably formed from the *trans* isomer by stereomutation during the oxidation process.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE REDUCING ACTION OF THE GRIGNARD REAGENT. II. COMPARISON WITH THE EASE OF REMOVAL OF HYDROGEN BROMIDE FROM ALKYL BROMIDES AND WITH THE AMOUNT OF DIALKYLMAGNESIUM IN THE GRIGNARD REAGENT

BY C. R. NOLLER AND F. B. HILMER

RECEIVED FEBRUARY 8, 1932 PUBLISHED JUNE 6, 1932

The theory proposed by Hess and Rheinboldt[1] to account for the reducing action of certain alkylmagnesium halides is that a primary addition product with the carbonyl compound is first formed and that this may either rearrange to give the normal addition product or may lose unsaturated hydrocarbon and then rearrange to give the reduction product.

$$R_2C{=}O + R'MgX \longrightarrow$$

$$R_2C{=}O\ldots Mg(X)R' \begin{cases} \nearrow R_2C(OMgX)R' \\ \searrow R'{-}H(\text{alkene}) + R_2C{=}O\ldots Mg(X)H \end{cases} \longrightarrow R_2C(OMgX)H$$

I II

Meisenheimer[2] proposed a similar mechanism except that the postulation of the intermediate compound II is omitted.

One might predict, if Hess' formulation represents the mechanism of the reaction, that for a series of alkylmagnesium halides the relative ease with which unsaturated hydrocarbon is lost from the complex $R_2CO\ldots Mg(X)R'$ and hence the relative amount of reduction might be comparable with the relative ease with which alkenes are formed from alkyl halides. A rough evaluation of the relative ease with which pyridine reacts with alkyl bromides to form alkene and pyridine hydrobromide has been reported recently[3] and it is the purpose of this paper to present data on the amount of reduction brought about by Grignard reagents from these same alkyl

[1] Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921).

[2] Meisenheimer, *Ann.*, **442**, 180 (1925).

[3] Noller and Dinsmore, THIS JOURNAL, **54**, 1025 (1932).

bromides. At the same time data on the amount of dialkylmagnesium in the Grignard reagent will also be given.

The method of Blicke and Powers[4] for estimating the amount of reduction, which is based on the insolubility of the bromomagnesium salt of benzohydrol in ether, is probably the most satisfactory for comparing the reducing action of various reagents. Their data, however, are not sufficiently complete to compare with the data on the relative ease of formation of alkenes from alkyl bromides. We have made use of their method and extended their data taking the precautions to use filtered solutions, to use solutions of the same concentration and in definite excess, and to carry the reaction out within the narrow temperature range of 0–5°.[5]

The amount of dialkylmagnesium in the solutions was determined by a modification[6] of the method of Schlenk and Schlenk, Jr.[7] The combined data are summarized in Table I which gives the average values of at least two determinations.

The work on the reaction of alkyl bromides with pyridine[3] showed that *tert.*-butyl bromide loses hydrogen bromide about eighty times more rapidly than the secondary bromides, isopropyl and *sec.*-butyl, and these in turn about ten times more rapidly than the primary bromides, ethyl, *n*-propyl, isobutyl and *n*-butyl. On comparing this order with that given in Table I, it is readily seen that there is no observable relation between the amount of reduction and the ease with which alkenes are formed from alkyl bromides.

On the other hand, it appears that the amount of reduction increases with increasing dialkylmagnesium content of the solution. There is, however, no direct relationship between the two since the *tert.*-butyl solution causes no reduction although there is 32 equivalent per cent. of dialkylmagnesium present, the isobutyl solution causes 86% reduction although only 78% of dialkylmagnesium is present, and the isopropyl and *sec.*-butyl solutions have almost the same dialkylmagnesium content but cause 13 and 40% reduction, respectively. None of the explanations that have suggested themselves will satisfy the data obtained thus far.

Our modification[6] of the excellent method used by Schlenk and Schlenk, Jr.,[7] for determining the amount of dialkylmagnesium is by no means as exact as theirs but the greater ease of carrying out the determination and its applicability to solutions of the Grignard reagent as directly pre-

[4] Blicke and Powers, THIS JOURNAL, **51**, 3378 (1929).

[5] The necessity for using filtered solutions and for keeping the Grignard reagent in excess have been reported in a previous paper.[6] Rheinboldt and Roleff, *J. prakt. Chem.*, **109**, 175 (1925), have shown that the amount of reduction increases with the temperature, and we have reason to believe that the amount of reduction also varies with the concentration of the Grignard reagent.

[6] Noller, THIS JOURNAL, **53**, 635 (1931).

[7] Schlenk and Schlenk, Jr., *Ber.*, **62**, 920 (1929).

pared give it certain advantages. In the two instances where a direct comparison is possible the two methods check fairly well. Thus Schlenk, Jr.,[8] finds for ethylmagnesium bromide solutions 29.5% diethylmagnesium and for *n*-propylmagnesium bromide 38% of di-*n*-propylmagnesium as compared with our values of 25.5 and 35.5%, respectively.

It appears that the generalization of Schlenk, Jr., that the amount of dialkylmagnesium increases with increasing molecular weight, must be modified to take the structure of the hydrocarbon radical into consideration. Our results for example indicate that the amount of dialkylmagnesium in the solution of *tert.*-butylmagnesium bromide is lower than that in any of the Grignard reagents including the ethyl and propyl solutions.

Experimental

Grignard Reagents.—Solutions of the alkylmagnesium bromides were prepared in the usual manner from purified alkyl bromides and filtered by pressure through a 3-mm. layer of ignited kieselguhr on a sintered glass filter. They were analyzed by titration with standard acid and then concentrated or diluted to give a concentration of approximately 1.75 *N*, after which the concentration was checked again by titration.

Reduction Procedure.—To a 300-cc. Erlenmeyer flask fitted with a 30-cc. dropping funnel and thermometer was added 25 cc. of the Grignard reagent. The solution was cooled to 0° in an ice–salt bath. The amount of benzophenone to be used was calculated for the particular Grignard reagent so that the latter was present in 10% excess, and this amount dissolved in 8 cc. of warm dry benzene. This solution was added dropwise from the separatory funnel at such a rate that the temperature remained between 0 and 5°. The contents of the flask was swirled continuously to keep the mixture well stirred.[9] When all the benzophenone had been added the contents of the flask was allowed to come to room temperature. The precipitate was filtered with suction on a 5-cm. Büchner funnel and washed carefully with three 10-cc. portions of dry benzene, care being taken not to suck air through the precipitate before the last washing. The cake was transferred to the Erlenmeyer flask, decomposed with 50 cc. of saturated ammonium chloride solution and extracted with three 50-cc. portions of ether. The combined ether extracts were evaporated in a tared 150-cc. beaker over a warm hot-plate. To prevent benzohydrol from creeping over the edge of the beaker, the ether vapors were removed by a tube attached to a water pump and extending into the center of the beaker. When practically all of the ether and benzene had been removed, the warm beaker was placed in a vacuum desiccator over phosphorus pentoxide, the desiccator evacuated and allowed to stand for two hours. The amount of benzohydrol was weighed and the percentage reduction calculated.

In checking the accuracy of the method we have determined roughly the solubility of the bromomagnesium salt of benzohydrol in ether, benzene and ether–benzene mixtures (25:8 by volume) and obtained the values 0.006, 0.007 and 0.006 g. per cc. of solution, which corresponds to 0.0038, 0.0045 and 0.0038 g. of benzohydrol. This solubility does not account for the fact that Blicke and Powers[4] recovered only 81% of the

[8] Schlenk, Jr., *Ber.*, **64**, 734 (1931).

[9] In all cases the usual transient red color was observed. In the case of *sec.*-butylmagnesium bromide, however, the color was permanent for as long as two weeks and was not destroyed by passing air through the solution for ten minutes. The *tert.*-butylmagnesium bromide likewise gave a permanently colored solution.

benzohydrol added to a solution of ethylmagnesium bromide. On repeating their work with 7.54 g. of freshly recrystallized benzohydrol, m. p. 66–67°, under exactly the same conditions used for determining the amount of reduction, we recovered 7.24 g. or 96% of the benzohydrol, m. p. 62–66°, from the precipitate and 0.26 g. or 3.4% from the filtrate. This indicates a mechanical loss of 0.6%. The value of 0.26 g. in the filtrate checks very closely with the calculated value of 0.27 g. based on the solubility determinations. This indicates that the values for the amount of reduction are low by about 4%.

Determination of Dialkylmagnesium.—The procedure was identical with that previously reported.[6]

All data are tabulated in Table I.

TABLE I

COMPARISON OF AMOUNT OF REDUCTION WITH DIALKYLMAGNESIUM CONTENT OF THE GRIGNARD REAGENT

Alkylmagnesium bromide	Concentration, equiv. per cc.	Dialkylmagnesium, equiv., %	Benzohydrol, %	M. p. of Benzohydrol, °C.
Tert.-butyl	0.00172	32	0[10]	
Ethyl	.00175	51	2	50–70
Isopropyl	.00165	59	13	61–63
Sec.-butyl	.00183	62	40	61–64
n-Propyl	.00179	71	58	60–63
n-Butyl	.00177	74	59	61–64
Isobutyl	.00174	78	86	62–66

Summary

1. Comparison of the amount of reduction of benzophenone by Grignard reagents from seven alkyl bromides with data on the relative ease with which alkenes are formed from these bromides shows that no relationship between the two exists.

2. The amount of reduction increases with the increasing dialkylmagnesium content of the solutions but is not proportional to the amount of dialkylmagnesium present.

3. The amount of dialkylmagnesuim present in Grignard solutions appears to be influenced more by the structure than by the molecular weight of the hydrocarbon radical.

STANFORD UNIVERSITY, CALIFORNIA

[10] From 7.1 g. of benzophenone there was obtained 7.1 g. of a viscous liquid distilling almost completely between 155–160° at 4 mm. Marvel and Bateman, THIS JOURNAL, **49**, 2917 (1927), give the b. p. of *tert.*-butyldiphenylcarbinol as 148–150° at 2.5 mm. This behavior of *tert.*-butylmagnesium bromide is surprising since Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929), found that in general *tert.*-butylmagnesium chloride caused more reduction than either isopropyl or *n*-butylmagnesium bromide and Konovalov, Miller and Timtschenko, *Chem. Zentr.*, II, 312 (1906), have obtained 38.5% benzohydrol from the reaction of benzophenone with *tert.*-butylmagnesium bromide. We believe that these apparent discrepancies may be due to variation in the conditions under which the reaction takes place, *cf.* Note 5.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE NITRATION OF THE METHYL, ETHYL AND TERTIARY-BUTYL ESTERS OF PHENYLACETIC ACID

BY DAVID L. YABROFF AND C. W. PORTER

RECEIVED FEBRUARY 15, 1932 PUBLISHED JUNE 6, 1932

This paper deals with the nitration of three of the esters of phenylacetic acid. The work reported here is a continuation of an investigation of the orienting influences of various groups in the benzene ring. The purpose of the research was formulated in an earlier paper.[1] In general it is an attempt to evaluate the orienting influences of atoms and groups not directly attached to the ring. The residual charge on the key atom in phenylacetic acid and its esters as estimated by Latimer and Porter[2] is zero; that in toluene is also zero. In benzoic acid and its esters the residual charge on the atom attached to the ring is +1.4.

Table I gives our results for the nitration of phenylacetic acid[1] and its esters and Zaki's results[3] for the three esters of benzoic acid. The values for toluene[4] and for benzoic acid[5] are those of Holleman.

TABLE I

Nitration of	Meta, %	Nitration of	Meta, %
$C_6H_5CH_2COOH$	14.4	C_6H_5COOH	80.2
$C_6H_5CH_2COOCH_3$	12.1	$C_6H_5COOCH_3$	72.6
$C_6H_5CH_2COOC_2H_5$	10.3	$C_6H_5COOC_2H_5$	69.9
$C_6H_5CH_2COOC(CH_3)_3$	5.6	$C_6H_5COOC(CH_3)_3$	59.4
$C_6H_5CH_3$	4.4		

As may be seen in Table I the percentage of the meta derivative is highest in the case of the free acid. Replacement of the hydrogen by alkyl groups causes a successive diminution in the percentage of the meta isomer. This was explained by Zaki[3] for the benzoic esters as due to the electron affinity of the various alkyl groups as compared with that of hydrogen. In our language we should say that the replacement of hydrogen by the various alkyl groups must modify the residual charge on the key atom. In the case of the esters the effective residual charge must be slightly more negative than that of the free acid, since less of the meta derivative is formed.

Methyl phenylacetate and tertiary-butyl phenylacetate heretofore have not been nitrated although nitro derivatives of the methyl ester have been obtained by esterification of the corresponding nitrophenylacetic

[1] Yabroff and Porter, THIS JOURNAL, **54**, 1199 (1932).

[2] Latimer and Porter, *ibid.*, **52**, 206 (1930).

[3] Zaki, *J. Chem. Soc.*, 983 (1928).

[4] Holleman, *Rec. trav. chim.*, **33**, 1 (1914).

[5] Holleman, *ibid.*, **18**, 278 (1899).

acids.[6,7,8] Tertiary-butyl phenylacetate was included in order to ascertain the accentuated effect of the three methyl groups in the alcohol residue. Ethyl phenylacetate has been nitrated by Baker and Ingold,[9] who found that approximately 9% of the meta derivative was formed and by Flürscheim and Holmes,[10] who obtained about 12% of the meta isomer.

The analytical method used for determining the percentage of the meta derivative for the three esters of phenylacetic acid was the same as that described for phenylacetic acid itself.[1]

Experimental Section

Reagents.—Eastmans ethyl and methyl phenylacetates were purified by fractional distillation under reduced pressure. The preparation and purification of tertiary-butyl phenylacetate has been described.[11]

Nitration.—The methyl and ethyl esters were nitrated by adding approximately 5 g. of the purified ester in small amounts to 30 cc. of nitric acid (*d* 1.495) freed from oxides of nitrogen. The temperature was maintained at 0° and the flask was thoroughly shaken after each small addition of the ester. The mixtures were allowed to stand for four hours longer at 0°.

Attempts to nitrate the tertiary-butyl ester in the same manner led to a great amount of hydrolysis (60–80%). Nitration was finally accomplished by allowing a mixture of 25 cc. of nitric acid (*d* 1.52) and 25 cc. of acetic anhydride to run slowly into a solution of the ester (about 7 g.) in 30 cc. of acetic anhydride. The temperature was maintained at 0°. The nitric acid solution was added at a steady rate of about 1 cc. per minute and the mixture was stirred vigorously during the entire time of addition. The mixture was then allowed to stand for one and one-half hours longer at 0°.[12]

After the period of nitration was over the nitration mixture obtained from each ester was poured into cracked ice and just neutralized with potassium hydroxide solution. The temperature was maintained at 0° by the further addition of ice. The nitro bodies which separated as a semi-solid oil were taken up with ether and the aqueous layer was extracted twice with ether. The ether extracts were combined, washed with ice water and dried over anhydrous sodium sulfate. Evaporation of the ether left a very pale yellow oil which became semi-solid upon standing. Equivalent weight determinations and analyses were made as described in the earlier paper.[1]

The results of the nitrations and analyses are given in Tables II, III and IV where the figures for the molecular weights, the titrations and the brominations represent averages of three determinations made with aliquot

[6] Maxwell, *Ber.*, **12,** 1764 (1879).

[7] Bedson, *J. Chem. Soc.*, **37,** 90 (1880).

[8] Borsche, *Ber.*, **42,** 3596 (1909–1910).

[9] Baker and Ingold, *J. Chem. Soc.*, 832 (1927).

[10] Flürscheim and Holmes, *ibid.*, 1607 (1928).

[11] Yabroff and Porter, THIS JOURNAL, **54,** 2453 (1932).

[12] The use of a solvent, such as acetic anhydride, may change the total rate of nitration, but if the solvent does not react with the compound which is being nitrated, the ratios between the ortho, meta and para derivatives remain constant. For evidence relating to this assumption see Holleman, *Chem. Rev.*, **1,** 224 (1925), and Francis, *ibid.*, **3,** 257 (1927).

parts of the sample. The weights referred to in the tables are in grams. For a complete explanation of the headings used in the following tables see our first paper.[1] To avoid unnecessary duplication the details of the procedure are not presented here.

TABLE II

METHYL PHENYLACETATE

	1	2	3
Nitration number			
Weight nitrated	4.83	5.64	4.93
Weight of nitro compounds obtained	5.70	7.04	6.01
Nitration yield, %	91	96	94
Molecular weight of nitration product	195.3	195.7	195.0
Weight oxidized by $KMnO_4$	4.57	4.82	4.61
Weight of oxidation products obtained (benzoic and nitrobenzoic acids)	3.56	3.67	3.55
Oxidation yield, %	91	89	90
Weight of benzoic acid sublimed	0.024	0.021	0.051
Benzoic acid present in product, %	0.7	0.6	1.4
Molecular weight of oxidation products	167.1	167.0	167.4
0.2485 N $TiCl_3$ required to reduce the sample, cc.	30.60	30.83	29.33
Total nitrobenzoic acids present, g	0.2117	0.2133	0.2029
Tribromoaniline formed from reduced sample including solubility correction, g	0.367	0.372	0.351
o-p-Nitrobenzoic acids present, g	0.1859	0.1884	0.1778
Meta compound, %	12.2	11.7	12.4

Average percentage of meta compound, 12.1

TABLE III

ETHYL PHENYLACETATE

	1	2	3
Nitration number			
Weight nitrated	4.63	5.21	4.97
Weight of nitro compounds obtained	5.62	6.45	5.82
Nitration yield, %	95	97	92
Molecular weight of nitration product	207.0	209.3	208.6
Weight oxidized by $KMnO_4$	4.60	4.53	4.56
Weight of oxidation products obtained (benzoic and nitrobenzoic acids)	3.30	3.27	3.20
Oxidation yield, %	90	90	88
Weight of benzoic acid sublimed	0.016	0.037	0.029
Benzoic acid present in product, %	0.5	1.1	0.9
Molecular weight of oxidation products	167.2	166.9	166.8
0.2485 N $TiCl_3$ required to reduce the sample, cc.	30.12	31.61	27.98
Total nitrobenzoic acids present, g	0.2084	0.2187	0.1936
Tribromoaniline formed from reduced sample including solubility correction, g	0.370	0.386	0.343
o-p-Nitrobenzoic acids present, g	0.1874	0.1955	0.1737
Meta compound, %	10.1	10.6	10.3

Average percentage of meta compound, 10.3

TABLE IV

TERTIARY-BUTYL PHENYLACETATE

Nitration number	1	2	3
Weight nitrated	6.46	6.88	6.56
Weight of nitro compounds obtained	7.39	7.55	7.90
Nitration yield, %	93	89	98
Molecular weight of nitration product	239.3	238.1	237.8
Weight oxidized by $KMnO_4$	5.13	4.86	4.75
Weight of oxidation products obtained (benzoic and nitrobenzoic acids)	3.15	3.04	3.10
Oxidation yield, %	87	89	93
Weight of benzoic acid sublimed	0.038	0.027	0.016
Benzoic acid present in product, %	1.2	0.9	0.5
Molecular weight of oxidation products	166.9	167.3	167.1
0.2507 *N* $TiCl_3$ required to reduce the sample, cc.	32.48	30.81	32.83
Total nitrobenzoic acids present, g.	0.2267	0.2151	0.2292
Tribromoaniline formed from reduced sample including solubility correction, g.	0.421	0.400	0.429
o–*p*-Nitrobenzoic acids present, g.	0.2133	0.2026	0.2173
Meta compound, %	5.9	5.8	5.2

Average percentage of meta compound, 5.6

Summary

As a continuation in the study of the influences of remote atoms on the residual charge of the key atom in benzene derivatives, the quantitative nitration of the methyl, ethyl and tertiary-butyl esters of phenylacetic acid has been accomplished. The percentages of the meta derivatives formed were 12.1, 10.3 and 5.6, respectively.

BERKELEY, CALIFORNIA

[CONTRIBUTION NO. 232 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

NITRATION OF META-DIPHENYLBENZENE AND DERIVATIVES OF NITRO-META-DIPHENYLBENZENE[1]

BY C. ARTHUR WARDNER WITH ALEXANDER LOWY

RECEIVED FEBRUARY 20, 1932 PUBLISHED JUNE 6, 1932

In the process for the preparation of diphenyl from benzene, considerable amounts of high boiling products are produced. *m*-Diphenylbenzene is one of the constituents of this high boiling material. Since the trinitro compound is the only nitro derivative of *m*-diphenylbenzene which has been recorded, a study of the nitration of this hydrocarbon was undertaken with the object of synthesizing the mono and dinitro compounds and some of their derivatives.

[1] Abstracted from a thesis presented by C. Arthur Wardner to the Graduate School in partial fulfilment of the requirement for the Ph.D. degree.

References to the literature[2] deal mainly with the preparation of *m*-diphenylbenzene from various sources.

The only derivatives which have been recorded for this hydrocarbon are the trinitro, triamino, bromo and tetrabromo compounds.

The writers are indebted to Mr. R. E. Bowman of Wilmington, Delaware, who is investigating the high boiling material furnished by the Swann Corporation, for providing a generous supply of *m*-diphenylbenzene. The *m*-diphenylbenzene thus obtained was recrystallized twice from ethyl alcohol, producing white needle-shaped crystals, m. p. 85°, as reported by Schultz, Schultz and Schmidt, Olgiati, Adam, Möhlun and Berger, Chattaway and Evans.[2] *m*-Diphenylbenzene is described in Beilstein[3] as white needle-shaped crystals. It is soluble in ethyl alcohol, ethyl ether, benzene and acetic acid. It boils at 363° under atmospheric pressure.

Several preliminary experiments were conducted, in which such factors as time, concentration of nitrating agent, temperature and solvent were varied, before the following procedures were adopted.

A. Nitration of *m*-Diphenylbenzene

Nitro-*m*-diphenylbenzene.—Fifty grams of *m*-diphenylbenzene and 200 cc. of acetic anhydride were mixed thoroughly with a mechanical agitator in a 600-cc. beaker until a uniform suspension was obtained and then cooled to 0°; 17.5 cc. of fuming nitric acid (sp. gr. 1.5) was added drop by drop with continuous stirring in the course of twenty minutes. As the reaction proceeded, the *m*-diphenylbenzene gradually dissolved. The same low temperature was maintained for fifteen minutes after the last drop of fuming nitric acid had been added. The solution was then warmed gradually to a temperature of 25°, which required twenty minutes. To ensure complete nitration, the reaction mixture was heated at 50° for thirty minutes.

The oily nitro compound separated as a distinct layer at the bottom when the nitrating mixture was poured into 500 cc. of ice water. The water layer was decanted and the nitro compound was washed with 500 cc. of warm water (temp. 50°). This was followed by several washings with warm five per cent. sodium carbonate solution. It was then washed with warm water. The oily product was dissolved in 150 cc. of ethyl ether and the resulting solution was dried over calcium chloride for twelve hours. The solution was filtered and the solvent was removed. The residual oil was vacuum distilled and the portion boiling at 197–198° (1 mm.) or 203° (2 mm.) was collected; yield, 36 g.

Attempts to crystallize this nitro compound were futile. Although it could be frozen to a solid with carbon dioxide snow, it acquired the characteristic viscous property when it warmed to room temperature. A portion of the nitro compound was kept in a refrigerator, while another portion was kept in a vacuum desiccator for ten months but there was no crystal formation in either of these samples.

---

[2] Schultz, *Ann.*, **174**, 228 (1874); Schultz and Schmidt, *ibid.*, **203**, 118 (1880); Olgiati, *Ber.*, **27**, 3385 (1894); Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927); Chattaway and Evans, *J. Chem. Soc.*, **69**, 980 (1896); Adam, *Ann. chim. phys.*, [6] **15**, 224 (1888); Möhlun and Berger, *Ber.*, **26**, 1994 (1893); Mannich, *ibid.*, **40**, 159 (1907); Gastaldi and Cherchi, *Gazz. chim. ital.*, **45**, II, 251 (1915).

[3] Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. V, System No. 450–498, p. 695.

Experiments were also conducted to crystallize the nitro compound from organic solvents. It was dissolved in ethyl ether, benzene, acetic acid and acetone, but these solvents did not affect crystallization, even after the solutions were concentrated and cooled. The nitro compound is insoluble in water.

Anal. Calcd. for $C_{18}H_{13}O_2N$: C, 78.54; H, 4.72; N, 5.09. Found: C, 78.00, 78.17; H, 4.50, 4.94; N, 5.03, 5.21.

Dinitro-*m*-diphenylbenzene.—A mixed acid solution was prepared, consisting of 30 cc. of sulfuric acid (sp. gr. 1.82), 15 cc. of nitric acid (sp. gr. 1.42) and 7.5 cc. of water. This mixture was kept at a constant temperature of 40° and stirred while 20 g. of *m*-diphenylbenzene was added in small portions, over a period of twenty minutes. A yellow oil formed which was insoluble in the nitrating acid. At this stage 10 cc. of nitric acid (sp. gr. 1.42) was added drop by drop. The product became pasty. The formation of this insoluble viscous product made further nitration almost impossible, and since higher temperature in this acid medium is conducive to oxidation, the operation was discontinued. The nitrating acid was decanted and the insoluble material was washed with cold water. The solid material thus obtained was crystallized from acetic acid, washed with water and dried. A yield of 14 g. was obtained, which had a melting point range of 160–190°. The product was crystallized six times from acetic acid, washed with water and dried in an oven at 80°; m. p. 214°; yield, 7. g. This product is soluble in acetic acid, benzene and acetone when heated.

Anal. Calcd. for $C_{18}H_{12}O_4N_2$: N, 8.75. Found: N, 8.76, 8.85.

The mother liquor from the first acetic acid crystallization was poured into 200 cc. of cold water. The oily material which separated was washed with water, dissolved in ether and the resulting solution was dried over calcium chloride for twelve hours. After filtration and evaporation of the solvent, a small amount of an oily liquid was obtained.

Trinitro-*m*-diphenylbenzene. 1. From *m*-Diphenylbenzene.—Five grams of *m*-diphenylbenzene and 25 cc. of acetic acid were mixed thoroughly in a 250-cc. round-bottomed flask; 16 cc. of fuming nitric acid (sp. gr. 1.5) was added in the course of one hour, while stirring and heating at 30°. The reaction mixture was heated for another hour on a boiling water-bath. A red coloration was noted in the solution at this point. Upon cooling, white needle-shaped crystals separated which were filtered by suction, washed with water and recrystallized three times from acetic acid. The resulting product was again washed with water and dried in an oven at 80°; m. p. 204°; yield, 4.5 g.; soluble in hot acetic acid, hot benzene and hot acetone, and slightly soluble in hot ethyl alcohol.

Anal. Calcd. for $C_{18}H_{11}O_6N_3$: N, 11.50. Found: N, 11.25, 10.96.

2. From Nitro-*m*-diphenylbenzene.—Five grams of nitro-*m*-diphenylbenzene was dissolved in 25 cc. of acetic acid in a 250-cc. round-bottomed flask; 16 cc. of fuming nitric acid (sp. gr. 1.5) was added slowly to the solution in the course of one hour, while the temperature was maintained at 25°. The temperature was raised gradually to 96–100°, where it was maintained for four hours. On cooling, white needle-shaped crystals separated, which were filtered and washed with water. These were crystallized three times from acetic acid; m. p. 204°; yield, 1 g.

The filtrate from the reaction mixture was poured into 250 cc. of cold water. A viscous semi-solid material separated, which was washed with water. This material was dissolved in ethyl ether and the solution dried over calcium chloride for twelve hours. One gram of a yellow solid separated. It was filtered but it could not be purified to a constant melting point by crystallization. Upon evaporation of the ether, a yellow oil having the appearance of the original mononitro derivative was obtained.

Oxidation of Nitro-*m*-diphenylbenzene.—Five grams of the nitro compound was dissolved in 25 cc. of acetic acid. To this solution while refluxing there was added a solution containing 40 g. of chromic acid in 40 cc. of acetic acid and 25 cc. of water in small quantities. After the last portion had been added, boiling was continued for one and a half hours. The reaction mixture was poured into 500 cc. of ice water, and the yellow precipitate which formed was filtered by suction and washed with water. It was dissolved in a 10% sodium hydroxide solution and reprecipitated with 1:1 hydrochloric acid. The resulting product was recrystallized twice from dilute ethyl alcohol (one part of alcohol to three parts of water). It was filtered by suction and dried in a vacuum desiccator; m. p. 224°. The product sublimed and this gave a melting point of 227°; yield, 0.9 g.

There are several possible oxidation products of nitro-*m*-diphenylbenzene, but only a few of these are recorded in the literature. The ones that are recorded with their respective melting points are as follows: 1-nitrobenzene-2,4-dicarboxylic acid, 245–246°; 1-nitrobenzene-3,5-dicarboxylic acid, 248–249°; 2-nitrobenzene-1,3-dicarboxylic acid, 300°; 2-nitrobenzoic acid, 148°; 3-nitrobenzoic acid, 140–141°; 4-nitrobenzoic acid, 238–240°.

The product obtained in the above oxidation experiment did not correspond with any of the compounds listed above. With the idea that one of these compounds might be obtained, the nitrodiphenylcarboxylic acid was subjected to a chromic acid oxidation for six hours more. However, the original acid was recovered. The product of oxidation is evidently a hitherto unreported nitrodiphenylcarboxylic acid.

Anal. Calcd. as nitrodiphenylcarboxylic acid ($C_{13}H_9O_4N$): N, 5.76; mol. wt., 243. Found: N, 5.51, 5.74; mol. wt. by titration of its neutral equivalent, 246.1, 245.9.

Oxidation of Dinitro-*m*-diphenylbenzene.—One gram of dinitro-*m*-diphenylbenzene was dissolved in 25 cc. of acetic acid. The procedure from this point was identical with that of the above oxidation experiment, except that the oxidizing agent consisted of 10 g. of chromic acid in 10 cc. of acetic acid and 5 cc. of water. White needle-shaped crystals formed which were recrystallized twice from water and dried in a vacuum desiccator; m. p. 238°; yield, 0.1 g. This melting point corresponds to that of *p*-nitrobenzoic acid. A mixed melting point indicated that the product was *p*-nitrobenzoic acid.

All attempts to oxidize the trinitro compound were futile, which is in accordance with the results of Schultz and Schmidt.[2]

Discussion of the above Results.—Theoretically, there are six mononitro derivatives of *m*-diphenylbenzene. Since in the nitration of diphenyl the ortho and para derivatives predominate, the mononitro products that would most likely form during the nitration of *m*-diphenylbenzene would be the following: (a) 2-nitro-5′-phenyl-diphenyl, (b) 4-nitro-5′-phenyl-diphenyl, (c) 1,3-diphenyl-2-nitrobenzene, (d) 1,3-diphenyl-4-nitrobenzene. The oxidation of nitro-*m*-diphenylbenzene yielded a hitherto unreported nitrodiphenylcarboxylic acid instead of a nitro-isophthalic acid or a nitrobenzoic acid, as would be expected. *o*-Nitrodiphenyl is not attacked by oxidizing agents while[4] *p*-nitrodiphenyl yields *p*-nitrobenzoic acid. This seems to indicate[5] that a phenyl group adjacent to a nitro group on a benzene nucleus is protected against oxidation. Reasoning by analogy from similar diphenyl type oxidations the formulas designated by (a) and

[4] Schultz, Schmidt and Strasser, *Ann.*, **207**, 348 (1881).

[5] Schultz, *ibid.*, **174**, 201 (1874).

(d) may be regarded as the two possible structures for nitro-*m*-diphenylbenzene, since a nitrodiphenylcarboxylic acid was isolated as an oxidation product.

The fact that *p*-nitrobenzoic acid was isolated as an oxidation product of dinitro-*m*-diphenylbenzene proves that a nitro group is attached in the para position on an end ring.

B. Derivatives of Nitro-*m*-diphenylbenzene

Amino-*m*-diphenylbenzene.—Ten grams of nitro-*m*-diphenylbenzene was dissolved in 30 cc. of ethyl acetate; 0.2 g. of platinum oxide, prepared according to the directions given in "Organic Syntheses,"[6] was used as a catalyst. The reduction was performed in a Parr catalytic hydrogenation machine. One hour was allotted for the completion of the reaction. The resulting solution was filtered to remove the platinum black. The solvent was removed and the resulting product was treated with 25 cc. of 1:5 hydrochloric acid. The white hydrochloride salt was filtered by suction, washed once with dilute hydrochloric acid and twice with 50 cc. of ethyl ether. The hydrochloride was then neutralized with a five per cent. solution of sodium carbonate. A small amount of ether was added to the mixture to dissolve the amine as it was formed. The ether was allowed to evaporate, and the amine separated in the form of a light gray solid. It was filtered and recrystallized three times from ethyl alcohol; m. p. 64°; yield, 6 g.; soluble in ethyl alcohol, ethyl ether, ethyl acetate, benzene and acetone.

Anal. Calcd. for $C_{18}H_{15}N$: N, 5.71. Found: N, 5.69, 5.81.

This product was also prepared by using the iron reduction method for reducing nitrodiphenyl.[7]

Amino-*m*-diphenylbenzene Hydrochloride.—One gram of amino-*m*-diphenylbenzene was dissolved in 20 cc. of ethyl acetate. This solution was agitated with dry hydrogen chloride gas until the amine had been precipitated as the white hydrochloride salt. It was filtered and dried in a vacuum desiccator.

Anal. Calcd. for $C_{18}H_{16}NCl$: N, 4.97. Found: N, 4.87, 4.80.

Acetylamino-*m*-diphenylbenzene.—One gram of amino-*m*-diphenylbenzene was dissolved in 5 cc. of acetic anhydride. The solution was heated for three minutes and then cooled. The addition of 5 cc. of water decomposed the excess acetic anhydride and caused the acetylated derivative to separate as a white solid. It was filtered by suction and recrystallized twice from 50% ethyl alcohol; m. p. 117°; yield, 1 g.

Anal. Calcd. for $C_{20}H_{17}ON$: N, 4.86. Found: N, 5.11, 4.96.

Benzoylamino-*m*-diphenylbenzene.—Two grams of amino-*m*-diphenylbenzene was dissolved in 5 cc. of pyridine. While stirring, three cc. of benzoyl chloride was added drop by drop. The reaction mixture became warm. On cooling, white needle-shaped crystals were deposited which were filtered by suction and washed with 0.5 *N* sulfuric acid. It was recrystallized from ethyl alcohol; m. p. 152°; yield, 2 g.

Anal. Calcd. for $C_{25}H_{19}ON$: N, 4.01. Found: N, 4.13, 3.78.

***m*-Diphenylbenzene-azo-β-naphthol.**—*m*-Diphenylbenzenediazonium chloride was prepared by diazotizing 2 g. of amino-*m*-diphenylbenzene hydrochloride in a solution of 100 cc. of distilled water and 10 cc. of hydrochloric acid (sp. gr. 1.18) at a temperature of 5°. This diazotized solution was poured slowly into a cooled solution containing 1.5

[6] Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

[7] Jenkins, McCullough and Booth, *Ind. Eng. Chem.*, **22**, 31 (1931).

g. of β-naphthol and 5 g. of sodium hydroxide in 100 cc. of water. A red precipitate formed, which was filtered by suction and washed with water. A red crystalline product was obtained after crystallization from acetic acid; yield, 2 g.

Anal. Calcd. for $C_{28}H_{20}ON_2$: N, 7.00. Found: N, 6.67, 6.86.

Other compounds were also coupled qualitatively with *m*-diphenylbenzenediazonium chloride, *e. g.*: 1,8-dihydroxynaphthalene-3,6-disulfonic acid, red-purple; 1-naphthol-4-sulfonic acid, bright red; 1,8-aminonaphthol-3,6-disulfonic acid, blue-purple; 2-naphthol-7-sulfonic acid, bright red; 1,8-aminonaphthol-2,4-disulfonic acid, purple; 2-naphthol-3,6-disulfonic acid, light purple.

Summary

1. The mononitro, dinitro and trinitro derivatives of *m*-diphenylbenzene have been prepared.

2. The oxidation of nitro-*m*-diphenylbenzene yielded a nitrodiphenylcarboxylic acid. The oxidation of dinitro-*m*-diphenylbenzene yielded *p*-nitrobenzoic acid. No reaction was observed in the attempted oxidation of trinitro-*m*-diphenylbenzene.

3. The nitro-*m*-diphenylbenzene was reduced to the corresponding amine. The following new derivatives of amino-*m*-diphenylbenzene were prepared: (a) amino-*m*-diphenylbenzene hydrochloride, (b) acetylamino-*m*-diphenylbenzene, (c) benzoylamino-*m*-diphenylbenzene, (d) *m*-diphenylbenzene-azo-β-naphthol, and other dyes.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PHENYL SUBSTITUTED ALIPHATIC ACIDS

BY J. HARMON AND C. S. MARVEL

RECEIVED FEBRUARY 25, 1932 PUBLISHED JUNE 6, 1932

The mechanism of the oxidation of the fatty acids in the animal body has long been the subject of speculation by chemists interested in metabolism. The most satisfactory theory that has been advanced to account for the oxidation of fatty acids to carbon dioxide and water in the animal was propounded by Knoop[1] in 1904. His theory of beta oxidation has been tested on various omega substituted fatty acids of the type $C_6H_5(CH_2)_xCOOH$ where the phenyl group which is not generally oxidized in the animal body acted as a barrier to further oxidation and left an identifiable residue to be eliminated as a waste product from the body. In these studies all of those acids in which *x* had an uneven value were found to be burned in the body to phenylacetic acid and those in which *x* had an even value were burned to benzoic acid.

Thus far most of the experiments which have been devised to test Knoop's theory of β-oxidation have confirmed it. However, it has been

[1] Knoop, *Beitr. Chem. Physiol. Path.*, **6**, 150 (1905).

pointed out by Professor R. C. Corley[2] that only omega substituted acids in which the aliphatic chain is fairly short have been examined and he has suggested that a study of longer straight chain fatty acids with the phenyl group at different distances from the carboxyl group and not in the omega position would be of interest.

Several aliphatic acids containing a phenyl group substituted in other than the alpha or omega positions have been prepared previously. Eijkman[3] prepared γ-phenylvaleric acid by the action of γ-valerolactone on benzene in the presence of aluminum chloride. When he tried to prepare the same acid from Δ^4-pentenoic acid and benzene[4] he obtained a mixture of the γ- and δ-phenyl substituted acids. The same method has been used by other investigators but mixtures of isomers seem invariably to result.[5] For the purpose for which these compounds were desired it seemed essential that pure compounds of known structures should be available. Accordingly, procedures which are known to produce compounds of definite composition were used in this work.

The acids desired for metabolism studies were those with ten to eighteen carbon atoms and having the phenyl group on various even numbered positions beyond six. Since the natural fatty acids have an even number of carbon atoms most of the compounds were of this type. Only one compound with an odd number of carbons in the aliphatic chain was prepared. The compounds which were obtained in sufficient quantity for animal experiments were 6-phenyldecanoic acid, 8-phenyldodecanoic acid, 10-phenyltetradecanoic acid, 6-phenylpentadecanoic acid, 8-phenylhexadecanoic acid, 9-phenyloctadecanoic acid, and 10-phenyloctadecanoic acid.

The last two of these acids served a double purpose; for in addition to being made available for study in the physiological work, they were used to compare with the phenyloctadecanoic acid which Nicolet and deMilt[5b] and Schmidt[5c] have prepared from oleic acid and benzene in the presence of aluminum chloride. The two synthetic acids of known structures were solids whereas the acid prepared from oleic acid is an oil. Comparison of the physical properties of the acids and also of the *p*-bromophenacyl esters which are given in detail in the experimental part showed that the acid from oleic acid is a mixture of about equal parts of the 9- and 10-phenyloctadecanoic acids.

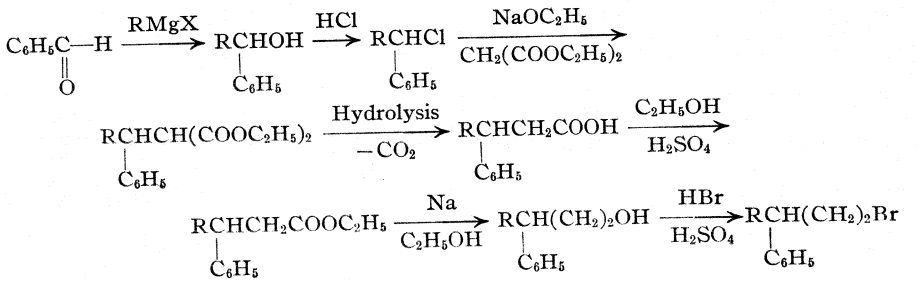
In the synthesis of these acids the first few reactions were of the same general type and may be represented as follows

[2] R. C. Corley in a private communication has suggested these facts to us and it was at his suggestion that this synthetic work was undertaken.

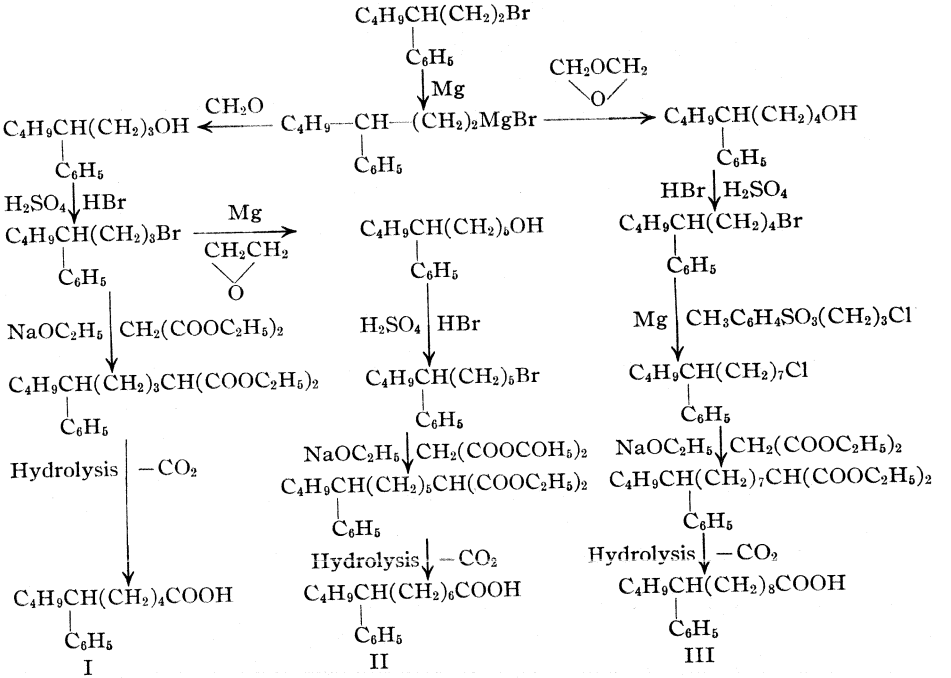
[3] Eijkman, *Chem. Weekblad*, **1**, 421 (1904).

[4] Eijkman, *ibid.*, **4**, 727 (1907).

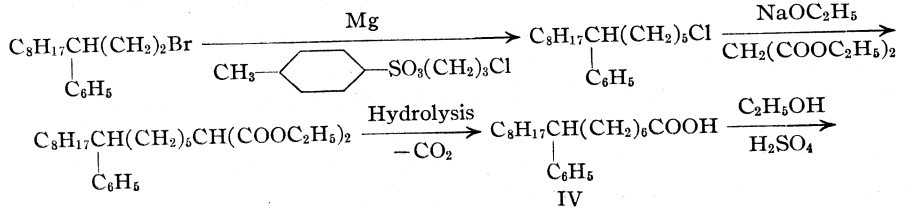
[5] (a) Eijkman, *ibid.*, **5**, 655 (1908); (b) Nicolet and deMilt, THIS JOURNAL, **49**, 1103 (1927); (c) Schmidt, *ibid.*, **52**, 1172 (1930); (d) Martin and Adams, private communication; (e) Fourneau and Baranger, *Bull. soc. chim.*, [4] **49**, 1161 (1931).

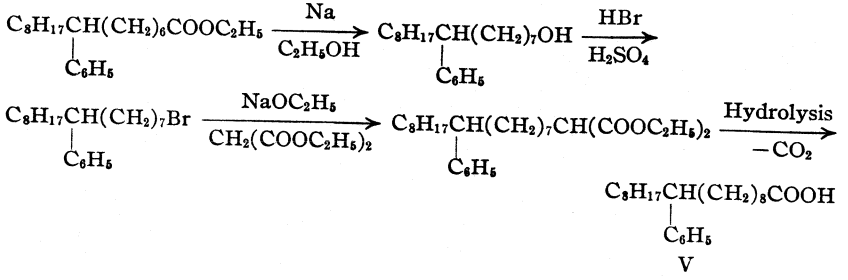


The reactions used in preparing 6-phenyldecanoic acid (I), 8-phenyldodecanoic acid (II) and 10-phenyltetradecanoic acid (III) are outlined below.

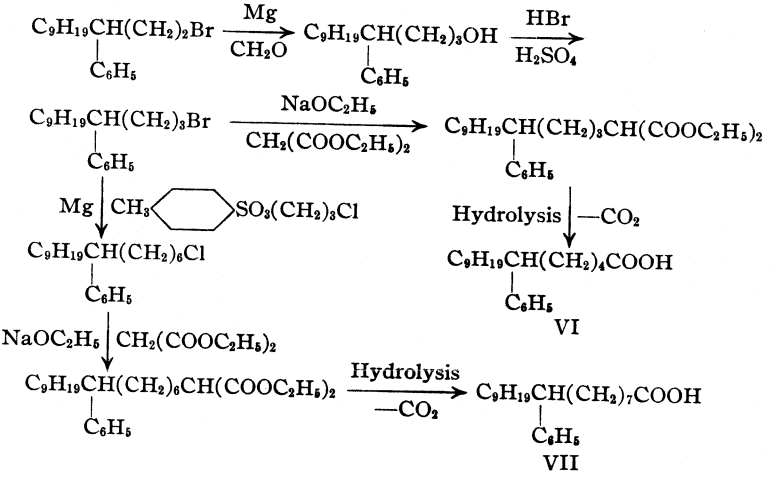


The methods of preparation used for 8-phenylhexadecanoic acid (IV) and 10-phenyloctadecanoic acid (V) are outlined below





The methods used for 6-phenylpentadecanoic acid (VI) and 9-phenyloctadecanoic acid (VII) are outlined in the following diagram



The alkyl phenyl carbinols and chlorides of the type $R-\underset{C_6H_5}{\underset{|}{C}}HOH$ and $R-\underset{C_6H_5}{\underset{|}{C}}HCl$, respectively, were not usually purified for use in further syntheses because they partially decomposed with the loss of water and hydrogen chloride, respectively, when an attempt was made to distil them. In the preparation of 6-phenyldecanoic acid an attempt was made to prepare the Grignard reagent from *n*-butylphenylchloromethane and to build up the chain by two methylene groups with ethylene oxide. The method could be used but it was not reliable and slight variations in the procedure which did not seem to be controllable resulted in a Würtz synthesis to give 5,6-diphenyldecane, and no Grignard reagent could be found. The malonic ester synthesis from the alkyl phenyl chloromethane gave about 75% yields on the average.

All of the other reactions were carried out according to the usual procedures described in the literature. Each of the new phenyl fatty acids

was characterized by the preparation of the *p*-bromophenacyl ester according to the procedure of Judefind and Reid.[6]

The results of the physiological experiments will be reported at a later date by Professor Corley.

Experimental Part

Grignard Reagents.—The Grignard reagents were prepared by the usual procedure using, on the average, seven moles of ether[7] per mole of alkyl halide. The ether was dried by distilling from ethylmagnesium bromide. The ether solution of the alkyl halide was added to the reaction mixture at such a rate as to cause very gentle refluxing.

Alkylphenylcarbinols.—The method of Conant and Blatt[8] for the preparation of alkylphenylcarbinols was applied to *n*-butylphenylcarbinol, *n*-octylphenylcarbinol and *n*-nonylphenylcarbinol. The *n*-butylphenylcarbinol, b. p. 97–104° (5 mm.), was obtained in the same yield which they have reported.

***n*-Octylphenylcarbinol.**—Several 2-mole runs of this alcohol were made and the yield of undistilled carbinol averaged 92% of the theoretical amount. It decomposed slowly on distillation under reduced pressure so that it was inadvisable to purify the product to be used in further work. A small sample was purified for analysis: b. p. 124–129° (3 mm.); n_D^{20} 1.4966; sp. gr.$_{25}^{25}$ 0.9238.

Anal. Subs., 0.2089: CO_2, 0.6237; H_2O, 0.2037. Calcd. for $C_{15}H_{24}O$: C, 81.75; H, 10.98. Found: C, 81.45; H, 10.85.

***n*-Nonylphenylcarbinol.**—The crude yield of this alcohol from a 2-mole run was 97% of the theoretical amount. The constants were determined on a purified sample: b. p. 121–124° (0.2 mm.); n_D^{20} 1.4953; sp. gr.$_{25}^{25}$ 0.9194.

Anal. Subs., 0.2224: CO_2, 0.6684; H_2O, 0.2223. Calcd. for $C_{16}H_{26}O$: C, 81.98; H, 11.19. Found: C, 81.97; H, 11.18.

Alkylphenylchloromethanes.—The alkylphenylcarbinols were converted to the chlorides by saturating with dry hydrogen chloride and heating the mixture. As a typical case dry hydrogen chloride was passed into 275 g. of crude carbinol contained in a 500-cc. gas washing bottle. Heat was generated and the carbinol at first became turbid and then two layers separated. When the reaction began to subside the bottle containing the reaction mixture was placed in a hot water-bath maintained at 60–70° and the current of dry hydrogen chloride was passed through the mixture about two hours longer. Ether was added to take up the chloride and the layers were separated. The ether solution was washed thoroughly with water and sodium bicarbonate solution to remove hydrogen chloride. It was then dried first over anhydrous magnesium sulfate, filtered and then dried over phosphorus pentoxide. The solution was again filtered and the ether was removed by distillation from a steam cone. The chloride was heated to 100° under 25 mm. pressure for a half an hour to remove low boiling impurities. Only *n*-butylphenylchloromethane was distilled under reduced pressure. The yield was 83% of the theoretical amount of a product; b. p. 84–87° (4 mm.); n_D^{20} 1.5125; sp. gr.$_{25}^{25}$ 0.9976. This material was not pure but contained some of the unsaturated hydrocarbon due to loss of hydrogen chloride. Chlorine analyses were about 1% too low. The other two chlorides were not distilled. The crude yields were 93% for the *n*-octyl derivative and 91% for the *n*-nonyl derivative.

---

[6] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

[7] (a) Gilman and McCracken, *Rec. trav. chim.*, **46**, 463 (1927); (b) Gilman and Zoellner, THIS JOURNAL, **50**, 425 (1928).

[8] Conant and Blatt, *ibid.*, **50**, 554 (1928).

Malonic Ester Synthesis.—All of the substituted malonic esters prepared in this work were made according to the method described in "Organic Syntheses"[9] except that the alcohol was dried with magnesium methylate[10] and the halide which was used was added more slowly (about 40–60 drops per minute). The reaction mixture was held at about 70° during the addition of the halide.

A record of the various preparations is given in Table I.

TABLE I

MALONIC ESTER SYNTHESES

Ester prepared	Halide	Halide, g.	Amount of malonic ester, g.	Yield, %
$C_4H_9CH(C_6H_5)CH(COOC_2H_5)_2$	Cl	365	342	75
$C_8H_{17}CH(C_6H_5)CH(COOC_2H_5)_2$	Crude Cl	476	372	56
$C_9H_{19}CH(C_6H_5)CH(COOC_2H_5)_2$	Crude Cl	252	171	61
$C_4H_9CH(C_6H_5)(CH_2)_3CH(COOC_2H_5)_2$	Br	107.6	64	66
$C_4H_9CH(C_6H_5)(CH_2)_5CH(COOC_2H_5)_2$	Br	44.5	26	67
$C_4H_9CH(C_6H_5)(CH_2)_7CH(COOC_2H_5)_2$	Cl	47.5	28	61
$C_9H_{19}CH(C_6H_5)(CH_2)_3CH(COOC_2H_5)_2$	Br	64	32	72
$C_8H_{17}CH(C_6H_5)(CH_2)_5CH(COOC_2H_5)_2$	Cl	167	92	42
$C_9H_{19}CH(C_6H_5)(CH_2)_6CH(COOC_2H_5)_2$	Cl	84	40	56.5
$C_8H_{17}CH(C_6H_5)(CH_2)_7CH(COOC_2H_5)_2$	Br	16.2	7.5	73

The physical constants and analyses of these esters are recorded in Table II.

TABLE II

CONSTANTS AND ANALYSES OF MALONIC ESTERS

R in R—$CH(COOC_2H_5)_2$	B. p., °C.	Mm.	n_D^{20}	Sp. gr.$^{25}_{25}$	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$C_4H_9CH(C_6H_5)$	143.5–147	3.5	1.4830	1.0401	$C_{18}H_{26}O_4$	70.54	8.56	70.43	8.64
$C_8H_{17}CH(C_6H_5)$	186–191	4	1.4816	0.9854	$C_{22}H_{34}O_4$	72.88	9.45	73.33	9.44
$C_9H_{19}CH(C_6H_5)$	163–166	0.3	1.4800	0.9831	$C_{23}H_{36}O_4$	73.35	9.63	73.34	9.59
$C_4H_9CH(C_6H_5)(CH_2)_3$	176–182	3	1.4812	1.0001	$C_{21}H_{32}O_4$	72.34	9.26	72.12	9.22
$C_4H_9CH(C_6H_5)(CH_2)_5$	185–190	3	1.4804	0.9911	$C_{23}H_{36}O_4$	73.35	9.63	72.94	9.48
$C_4H_9CH(C_6H_5)(CH_2)_7$	180–188	0.13	1.4800	.9735	$C_{25}H_{40}O_4$	74.20	9.96	74.14	9.99
$C_9H_{19}CH(C_6H_5)(CH_2)_3$	187–194	.13	1.4790	.9684	$C_{26}H_{42}O_4$	74.58	10.12	74.32	10.06
$C_8H_{17}CH(C_6H_5)(CH_2)_5$	205–211	.25	1.4788	.9634	$C_{27}H_{44}O_4$	74.94	10.26	75.00	10.32
$C_9H_{19}CH(C_6H_5)(CH_2)_6$	220–225	.2	1.4796	.9511	$C_{29}H_{48}O_4$	75.59	10.51	75.84	10.69
$C_8H_{17}CH(C_6H_5)(CH_2)_7$	217–224	.15	1.4780	.9560	$C_{29}H_{48}O_4$	75.59	10.51	75.77	10.53

Conversion of RMgX to RCH_2OH.—The reactions between the Grignard reagent and formaldehyde were carried out according to the procedure described in "Organic Syntheses."[11] The end of the reaction was noted by the fact that when all of the Grignard reagent had been used the ether ceased to reflux. No more formaldehyde was distilled into the reaction mixture after this drop in temperature of the reaction mixture was noted. The reaction mixture was decomposed with a small volume of saturated ammonium chloride solution and the alcohol was isolated by separating the ether solution, washing it with water and then drying with anhydrous magnesium sulfate. The ether was removed and the alcohol

[9] "Organic Syntheses," **4**, 11 (1924).

[10] "Organic Syntheses," **7**, 37 (1927).

[11] "Organic Syntheses," **6**, 22 (1926).

fractionated under reduced pressure. In each reaction of this type a high boiling residue of the acetal formed by the action of formaldehyde on the alcohol was left behind.[12] In the one case where this amounted to 34% of the total yield, hydrolysis to the desired alcohol was effected in 50% yield by refluxing it with alcoholic hydrogen chloride for twenty-two hours.

3-Phenyldodecyl bromide gave a 61% yield of 4-phenyltridecanol-1 and 11% of high boiling acetal which was not treated further.

3-Phenylheptyl bromide gave a 45% yield of 4-phenyloctanol-1 and 34% yield of acetal. This was hydrolyzed and the final yield of alcohol amounted to 62% of the theoretical amount. In the last preparation a low boiling fraction was isolated; b. p. 68–71° (3 mm.); sp. gr.$^{25}_{25}$ 0.8585; n^{20}_{D} 1.4871.

Anal. (3-Phenylheptane) Subs., 0.2092: CO_2, 0.6785; H_2O, 0.2132. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.48; H, 11.34.

The constants on the two new alcohols are given in Table III.

Conversion of RMgX to RCH_2CH_2OH.—The reactions between the Grignard reagents and ethylene oxide were carried out as described in "Organic Syntheses"[13] except that the reaction mixture was not allowed to heat much above 0° during the addition of ethylene oxide and after decomposition of the reaction mixture, the ether–benzene solution was thoroughly washed with water, dried over anhydrous magnesium sulfate and the solvent distilled. The residue was distilled under reduced pressure.

5-Phenylnonanol-1 was obtained in 55% of the theoretical amounts from 3-phenylheptyl bromide and 6-phenyldecanol-1 was obtained in 54% of the theoretical amount from 4-phenyloctyl bromide.

The constants of these alcohols are given in Table III.

TABLE III

CONSTANTS AND ANALYSES OF PHENYL ALKYL ALCOHOLS

Alcohol	B. p. °C.	Mm.	n^{20}_{D}	Sp. gr.$^{25}_{25}$	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
4-Phenyloctanol-1	125–130	3	1.5052	0.9405	$C_{14}H_{22}O$	81.49	10.75	81.31	10.72
4-Phenyltridecanol-1	158–160	0.14	1.4952	.9139	$C_{19}H_{32}O$	82.52	11.67	82.49	11.73
5-Phenylnonanol-1	137–144	0.94	1.5038	.9363	$C_{15}H_{24}O$	81.75	10.99	81.62	11.05
6-Phenyldecanol-1	140–144	3	1.5015	.9295	$C_{16}H_{26}O$	81.98	11.19	81.89	11.05

Preparation of Phenyl Alkyl Bromides.—The method used for preparing the bromides from the various alcohols was essentially that described in "Organic Syntheses"[14] for the higher alcohols. A mechanical stirrer was used on account of the low solubility of the alcohols. It was found necessary to reduce the amount of sulfuric acid to somewhat less than that used on the simple alcohols. The refluxing period was six to eight hours.

[12] Conant, "Organic Syntheses," **8**, 124 (1928); Conant, Webb and Mendum, THIS JOURNAL, **51**, 1246 (1929).

[13] "Organic Syntheses," **6**, 54 (1926).

[14] "Organic Syntheses," **1**, 7 (1921).

The bromides were purified by separating them from the mixture of sulfuric and hydrobromic acid, washing thoroughly with water and sodium bicarbonate solution, drying over anhydrous magnesium sulfate and distilling under reduced pressure. The once distilled bromide was then washed at 0° with small portions of 92.5% sulfuric acid. Stronger acid caused excessive charring and some sulfonation. After treating with five to six portions of sulfuric acid, the acid was no longer colored. This acid treatment had to be carefully done to avoid excessive loss. The bromide was then again washed, dried and distilled as before.

The results of these experiments are recorded in Tables IV and V.

TABLE IV

PREPARATION OF PHENYL ALKYL BROMIDES

Alcohol used	Amt., g.	48% HBr, g.	96% H_2SO_4, g.	Time of refluxing, hr.	Yield of bromide, %
3-Phenylheptanol-1	192	326	126	7.5	87
4-Phenyloctanol-1	206	326	126	7.5	91
5-Phenylnonanol-1	122	170	52	8	75
6-Phenyldecanol-1	112	156	61	7.25	82.5
3-Phenylundecanol-1	190	258	71	6	74
3-Phenyldodecanol-1	131	168	51	7	70
4-Phenyltridecanol-1	249	304	91	7	74
6-Phenylhexadecanol-1	27	29	8	8	57

TABLE V

CONSTANTS AND ANALYSES ON PHENYL ALKYL BROMIDES

Compound	B. p., °C.	Mm.	n_D^{20}	Sp. gr.$^{25}_{25}$	Formula	Br analyses, Calcd.	Found
3-Phenyl-1-bromoheptane	118–121	3	1.5215	1.1681	$C_{13}H_{19}Br$	31.35	31.37
4-Phenyl-1-bromooctane	124–126	3	1.5196	1.1490	$C_{14}H_{21}Br$	29.69	29.68
5-Phenyl-1-bromononane	125–127	2	1.5172	1.1260	$C_{15}H_{22}Br$	28.23	28.00
	140–145	4					
6-Phenyl-1-bromodecane	135–139	3	1.5150	1.1109	$C_{16}H_{25}Br$	26.89	26.89
3-Phenyl-1-bromoundecane	147–150	3	1.5090	1.0934	$C_{17}H_{27}Br$	25.69	25.40
3-Phenyl-1-bromododecane	141–147	0.15	1.5068	1.0770	$C_{18}H_{29}Br$	24.58	24.59
4-Phenyl-1-bromotridecane	150–155	.12	1.5061	1.0680	$C_{19}H_{31}Br$	23.56	23.62
8-Phenyl-1-bromohexadecane	169–172	.10	1.5015	1.0396	$C_{22}H_{37}Br$	20.96	20.97

Conversion of RMgX to $RCH_2CH_2CH_2Cl$.—The procedure used for converting the Grignard reagent to the alkyl chloride containing three more methylene groups was that described by Rossander and Marvel.[15] The yields were increased by avoiding an excess of magnesium in the solution of the Grignard reagent. The impure chlorides obtained by distilling once under reduced pressure and collecting a 20° fraction were purified by carefully washing with small portions of 92.5% sulfuric acid at 0°. Four or five extractions with acid were necessary. The chlorides were

[15] Rossander and Marvel, THIS JOURNAL, **50**, 1491 (1928).

then washed thoroughly with water and sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and distilled under reduced pressure.

The results of these experiments are collected in Table VI.

TABLE VI

PREPARATION OF PHENYL ALKYL CHLORIDES

Bromide used	G.	Wt. of γ-chloropropyl *p*-toluene sulfonate	Yield, %
5-Phenyl-1-bromononane	113.5	198.5	50
3-Phenyl-1-bromoundecane	215	354	54
4-Phenyl-1-bromotridecane	174	248	51.5

Compound prepared	B. p., °C.	Mm.	n_D^{20}	Sp. gr.$^{25}_{25}$	Cl analyses Calcd.	Found
8-Phenyl-1-chlorododecane	129–136	0.1	1.4974	0.9508	12.63	12.67
6-Phenyl-1-chlorotetradecane	166–173	3	1.4948	.9397	11.49	11.30
7-Phenyl-1-chlorohexadecane	160–165	0.1	1.4923	.9263	10.53	10.43

Preparation of Phenyl Fatty Acids.—All of the phenyl fatty acids were prepared by hydrolysis of the corresponding malonic esters followed by elimination of carbon dioxide. The esters were first saponified by adding one mole of ester to a hot solution of four moles of sodium hydroxide dissolved in alcohol. Four cc. of alcohol was used per gram of ester. The reaction was vigorous and the salt separated at once. When the ester had all been added, enough alcohol was added to make stirring efficient. The mixture was stirred occasionally and refluxed for about ten hours. The mixture was then evaporated to dryness in an open vessel on a steam cone. The salt was made into a paste with water and again evaporated to dryness in order to insure complete removal of the alcohol. The salt was then dried in an oven at 100–120°. The free organic acid was obtained by adding the powdered salt to an excess of hot 16% hydrochloric acid. Stirring was used during this operation. Then the mixture was heated until all of the precipitated organic acid had melted. After cooling the crude malonic acid which was thus formed was transferred to a Claisen flask and converted to the monocarboxylic acid by heating slowly to 190°. Sometimes it was necessary to use ether extraction to separate the organic dibasic acids from the aqueous acid in which they were precipitated.

After decomposition of the malonic acid, the mixture was cooled and the monobasic acid was taken up in ether. The ether solution was washed with water to remove all of the suspended salt and was then dried over anhydrous magnesium sulfate, and the ether was distilled. The residual acid was distilled under reduced pressure. A few of the acids were not purified (except for a small amount of material for analysis) but were used directly for other preparations.

A summary of these preparations is given in Table VII.

TABLE VII

PREPARATION AND PROPERTIES OF PHENYL FATTY ACIDS

Acid	% yield based on malonic ester	B. p. °C.	B. p. Mm.	n_D^{20}	Sp. gr.$^{25}_{25}$
3-Phenylheptanoic	Crude 96	144–149	3	1.5049	1.0117
6-Phenyldecanoic	90	176–180	3	1.5000	0.9817
3-Phenylundecanoic	Crude 99	167–172	2.5	1.4960	.9679
3-Phenyldodecanoic	Crude 99	165–171	0.3	1.4950	.9623
8-Phenyldodecanoic	82.5	184–187	3	1.4970	.9729
10-Phenyltetradecanoic	85	178–183	0.1	1.4936	.9555
6-Phenylpentadecanoic	92	182–185	.1	1.4924	.9470
8-Phenylhexadecanoic	Crude 99	190–195	.12	1.4912	.9417
9-Phenyloctadecanoic	84	200–204	.09	1.4891	.9340
		M. p. 36.5–38°			
10-Phenyloctadecanoic	90	199–205	0.09	1.4894	.9338
		M. p. 40–41.5°			

Formula	Neutral equivalent Calcd.	Neutral equivalent Found	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$C_{13}H_{18}O_2$	206.1	204, 207	75.68	8.80	75.57	8.85
$C_{16}H_{24}O_2$	248.2	246.2	77.36	9.74	77.39	9.71
$C_1\ H_{26}O_2$	262.2	270.2	77.80	9.94	77.89	9.98
$C_{18}H_{28}O_2$	276.2	278	78.17	10.21	77.69	10.12
$C_{18}H_{28}O_2$	276.2	269	78.17	10.21	78.05	10.05
$C_{20}H_{32}O_2$	304.2	306	78.88	10.60	78.84	10.74
$C_{21}H_{34}O_2$	318.3	321	79.18	10.77	79.29	10.87
$C_{22}H_{36}O_2$	332.3	338	79.45	10.92	79.44	10.96
$C_{24}H_{40}O_2$	360.3	363.4	79.93	11.19	79.77	11.03
$C_{24}H_{40}O_2$	360.3	360	79.93	11.19	80.03	11.20

Preparation of Ethyl Esters.—In certain cases these phenyl fatty acids were converted to the ethyl esters by the general procedure outlined in "Organic Syntheses"[16] except calcium oxide (small lumps) was used as the drying agent. It was renewed after about three hours in order to prevent violent bumping. The time allowed for esterification was about twenty

TABLE VIII

ETHYL ESTERS OF PHENYL FATTY ACIDS

Ethyl ester of acid	% yield based on malonic ester	B. p. °C.	B. p. Mm.	n_D^{20}	Sp. gr.$^{25}_{25}$
3-Phenylheptanoic	92	117–120	3	1.4859	0.9625
3-Phenylundecanoic	89	154–159	4	1.4823	.9360
3-Phenyldodecanoic	93	142–148	0.2	1.4827	.9289
8-Phenylhexadecanoic	90	174–180	.13	1.4808	.9194

Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$C_{15}H_{22}O_2$	76.87	9.42	76.85	9.49
$C_{19}H_{30}O_2$	78.55	10.42	78.67	10.47
$C_{20}H_{32}O_2$	78.88	10.60	79.19	10.66
$C_{24}H_{40}O_2$	79.93	11.19	80.00	11.30

[16] "Organic Syntheses," **5**, 59 (1925).

hours. To hasten the esterification about 12 cc. of concentrated sulfuric acid for each mole of organic acid was used as a catalyst. The ester was purified by distilling the excess alcohol, washing the residue with water and distilling under reduced pressure. The results of these preparations are summarized in Table VIII.

Reduction of Ethyl Esters to Primary Alcohols.—The reduction of the esters was carried out according to the general procedure described in "Organic Syntheses";[17] however, the details were varied considerably. About 0.4 mole runs were made using eight gram atoms of sodium per mole of ester and 290 cc. of absolute alcohol[9] per gram atom of sodium.

The sodium was cut into small pieces and placed in the flask under a little dry benzene. The ester was dissolved in about one-fifth of the total volume of ethyl alcohol in one separatory funnel and the remainder of the ethyl alcohol was placed in another separatory funnel. The benzene was warmed nearly to boiling, the alcohol solution of the ester was added all at once and just as the last of it ran in the stirrer was started and the alcohol from the other separatory funnel was added all at once. The sodium usually balled up into a large porous mass and was dashed back and forth in the solution by the stirrer. As soon as the initial vigorous reaction had subsided the reaction mixture was heated on a boiling water-bath and as soon as the sodium had dissolved the water-bath was removed and the hot sodium ethylate solution was decomposed by the cautious addition of a volume of water equal to about one-fourth the volume of the reaction mixture. The almost colorless solution was transferred to another flask and as much alcohol and benzene as possible was distilled from a steam cone. When more than one run was made it was advantageous to combine them at this point. After cooling, the layers were separated and the non-aqueous layer was taken up in an equal volume of ether and carefully washed with water several times. The ether solution was dried over anhydrous magnesium sulfate, filtered, the ether distilled and the residual alcohol was distilled under reduced pressure. The results of these experiments are summarized in Table IX.

TABLE IX

REDUCTION OF ESTERS

Alcohol prepared	Yield, %	B. p. °C.	Mm.	n_D^{20}	Sp. gr. $\frac{25}{25}$
3-Phenylheptanol-1	84	116–120	3	1.5070	0.9466
3-Phenylundecanol-1	74	139–145	2.5	1.4971	.9208
3-Phenyldodecanol-1	63.5	140–142	0.2	1.4959	.9169
8-Phenylhexadecanol-1	63	168–174	.1	1.4919	.9060
		M. p. 39–41°			

	Analyses, %			
	Calcd.		Found	
Formula	C	H	C	H
$C_{13}H_{20}O$	81.14	10.48	81.18	10.54
$C_{17}H_{28}O$	82.18	11.37	82.14	11.39
$C_{18}H_{30}O$	82.37	11.53	82.37	11.56
$C_{22}H_{38}O$	82.94	12.03	82.51	12.17

***p*-Bromophenacyl Esters of Phenyl Fatty Acids.**—The *p*-bromophenacyl esters of all of the phenyl fatty acids were prepared according to the method of Judefind and Reid.[6] The esters were crystallized from ethyl alcohol

[17] "Organic Syntheses," **10**, 62 (1930).

until the melting point was unchanged by further crystallization. Usually six to seven crystallizations were needed. The properties of the new derivatives are summarized in Table X.

TABLE X

p-BROMOPHENACYL ESTERS OF PHENYL FATTY ACIDS

p-Bromophenacyl ester of acid	M. p., °C.	Formula	Br analyses, % Calcd.	Found
3-Phenylheptanoic	47.4–48.2	$C_{21}H_{23}O_3Br$	19.83	19.79
6-Phenyldecanoic	55.5–56	$C_{24}H_{29}O_3Br$	17.95	17.89
3-Phenylundecanoic	65–65.5	$C_{25}H_{31}O_3Br$	17.40	17.34
3-Phenyldodecanoic	74.5–75.5	$C_{26}H_{33}O_3Br$	16.89	16.63
8-Phenyldodecanoic	89–90	$C_{26}H_{33}O_3Br$	16.89	16.86
10-Phenyltetradecanoic	79–80	$C_{28}H_{37}O_3Br$	15.95	16.14
6-Phenylpentadecanoic	73.5–74.5	$C_{29}H_{39}O_3Br$	15.49	15.53
8-Phenylhexadecanoic	77–78	$C_{30}H_{41}O_3Br$	15.10	15.03
9-Phenyloctadenoic	83.5–84.5	$C_{32}H_{45}O_3Br$	14.34	14.39
10-Phenyloctadecanoic	71–72	$C_{32}H_{45}O_3Br$	14.34	14.38

Phenylstearic Acid from Oleic Acid.—This acid was prepared according to the procedure of Nicolet and deMilt.[5b]

The *p*-bromophenacyl ester was prepared and it melted below 50° when first obtained. Crystallization from alcohol raised the melting point until finally after fourteen recrystallizations the melting point was 79–82°. To compare this acid with the pure samples of 9- and 10-phenyloctadecanoic acids prepared in this work, the properties of all these are summarized in Table XI.

TABLE XI

COMPARISON OF NICOLET AND DEMILTS' PHENYLSTEARIC ACID WITH KNOWN 9- AND 10-PHENYLOCTADECANOIC ACIDS

Acid	B. p., °C.	Mm.	M. p., °C.	n_D^{20}	Sp. gr.$^{25}_{25}$	M. p. of *p*-bromophenacyl ester, °C. Crude	Purified	Number of crystallizations
Phenyl stearic from oleic acid and benzene	199–203	0.08	Below 0	1.4906	0.9377	Below 50°	79–82	14
9-Phenyloctadecanoic	200–204	.09	36.5–38	1.4891	.9340	81–83	83.5–84.5	7
10-Phenyloctadecanoic	199–205	.09	40–41.5	1.4894	.9338	68–70	71–72	6

A mixture of equal parts of the *p*-bromophenacyl esters of the 9- and 10-phenyloctadecanoic acids melted at 65–73°. When the ester from Nicolet and deMilt's acid had been crystallized six times it melted at 66–73°. This seems to indicate that it is roughly an equal mixture of the two expected isomers.

Summary

1. Ten new phenyl substituted fatty acids have been prepared in order that certain of them could be used to test Knoop's beta oxidation theory for fatty acids.

2. The phenylstearic acid of Nicolet and deMilt has been compared with 9- and 10-phenyloctadecanoic acids and it has been found to be a mixture of approximately equal parts of these isomers.

3. A number of intermediate compounds used in the preparation of these compounds have been characterized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF THE CITY OF NEW YORK]

THE FATTY ACIDS ASSOCIATED WITH CASSAVA STARCH

BY LEO LEHRMAN

RECEIVED FEBRUARY 25, 1932 PUBLISHED JUNE 6, 1932

Some of the common cereal starches (corn, rice and wheat) have been shown to have fatty acids combined with carbohydrate in the α-amylose component.[1] The individual fatty acids found in each of these starches are the same though the amounts are different. Two tuber starches, cassava and potato, also contain combined fatty acids,[2] but in a much smaller percentage. Beyond this meager information no tuber starch has been investigated from the point of view of the combined fatty acids occurring in it. It would be important to know whether the fatty acids in a tuber starch such as cassava are the same as those found in the common cereal starches.

As in the investigations on the cereal starches a search for sterols and other substances that might occur in the starch and then be present in the liberated fatty acids must be made. This is necessary if there is to be any comparison of the fatty acids found in the different starches. It is also requisite to investigate the aqueous filtrate from the hydrolysis of the starch for glycerol to be sure that the fatty acids are not present in the starch as extraneous glycerides.

Experimental Part

Mixed Fatty Acids from Cassava Starch.—A sample of the cassava starch[3] was extracted with petroleum ether for several hours and showed a negligible amount of extractable material. The starch was hydrolyzed by hydrochloric acid[1b] in 2000-g. portions, a portion yielding 2 g. of a light yellow fatty semi-solid, equal to 0.1% "fat by hydrolysis" and having an iodine number of 78.8.[1a]

Examination of Filtrate for Glycerol.—Four liters of filtrate, dark brown in color, from the hydrolysis, was evaporated to 400 cc. of a thick sirupy liquid. As there is a great deal of frothing during the evaporation it was necessary to heat a volume not ex-

[1] (a) Taylor and Lehrman, THIS JOURNAL, **48**, 1739 (1926); (b) Lehrman, *ibid.*, **51**, 2185 (1929); (c) **52**, 808 (1930).

[2] Taylor and Nelson, *ibid.*, **42**, 1726 (1920).

[3] The author wishes to thank Stein, Hall and Co., Inc., New York City, for their kindness in supplying this material.

ceeding 500 cc. in a 2-liter beaker. To the thick sirupy liquid an equal volume of alcohol was added, stirred well and filtered. The dark brown filtrate was evaporated to dryness on the steam-bath. The residue was ground up, alcohol added, the mixture stirred well and filtered. The filtrate was again evaporated to dryness on the steam-bath. This procedure was repeated several times until a small amount of residue, dark brown in color, completely soluble in alcohol, was obtained. This solution gave a negative test for glycerol.[4]

Isolation and Identification of Saturated Fatty Acid.—In the course of the separation of the unsaturated fatty acids from the saturated by means of the magnesium soap–alcohol method,[5] the insoluble magnesium soap was decomposed by heating with concentrated hydrochloric acid. The liberated fatty material on purification[1c] yielded a white solid melting at 62°. The phenylhydrazide was made[6] and gave a melting point of 110°.[7]

The molecular weight of the acid was determined by dissolving a weighed amount in methyl alcohol and titrating with a standardized solution of barium hydroxide in methyl alcohol, using phenolphthalein as an indicator.[8]

Anal. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: mol. wt., 256.3. Mol. wt. found (monobasic acid), 248.

Anal. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: C, 74.91; H, 12.59. Found: C, 75.15; H, 12.44.

The above data indicate the presence of palmitic acid in the mixed fatty acids.

Identification of Unsaturated Fatty Acids. A. Oxidation.—The mixture of unsaturated fatty acids separated from the saturated fatty acid by means of the magnesium soap–alcohol method was a yellow oil having an iodine number of 100.6.[1a] When a solution of these unsaturated fatty acids in petroleum ether is chilled with an ice–salt mixture a small amount of solid forms. This was filtered off by suction while cold, washed with cold petroleum ether and allowed to dry. The dried solid has a cream color and melts at 70–71°. On account of the small amount no other data could be obtained.

A 2-g. portion of the unsaturated fatty acids was oxidized by potassium permanganate in alkaline solution.[9] The white solid oxidized acids, after being filtered off and allowed to dry, were extracted with chloroform in order to make a separation[1b] of the oxidized acids, if any. On evaporation of the chloroform a fatty material was obtained which was re-oxidized and gave a product different from the one obtained in the first treatment.

The solid oxidized acid (residue from the chloroform extraction) was extracted with hot water. The silky white solid obtained when the water cooled was redissolved in hot water and the solid allowed to crystallize out. This solid was filtered off and dried and gave a melting point of 155–156°.

Anal. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_6$: C, 62.02; H, 10.42. Found: C, 62.20; H, 10.23.

The data indicate the presence of linolic acid in the unsaturated fatty acids.

The product of the second oxidation was completely soluble in chloroform, showing the absence of tetrahydroxystearic acid. The chloroform solution was allowed to evaporate, yielding a white solid mixed with a small amount of fatty material. The

[4] Kolthoff, *Pharm. Weekblad*, **61**, 1497 (1924).

[5] Thomas and Yu, THIS JOURNAL, **45**, 123 (1923).

[6] Brauns, *ibid.*, **42**, 1480 (1920).

[7] J. van Alphen, *Rec. trav. chim.*, **44**, 1064 (1925).

[8] Escher, *Helv. Chim. Acta*, **12**, 103 (1929).

[9] Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

fatty material was removed with a little ether and the white residue dissolved by extraction with chloroform. On evaporation of the chloroform a white solid, m. p. 123–124°, was obtained.

Anal. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: C, 68.29; H, 11.47. Found: C, 68.39; H, 11.36.

These data indicate the presence of oleic acid in the unsaturated fatty acids.

The fact that no tetrahydroxystearic acid is found in the product of the second oxidation apparently indicates that it had been completely oxidized before the oleic acid.

The filtrate from the first oxidation was examined for higher hydroxy acids[10] but the results were negative, indicating the possible absence of acids more unsaturated than linolic in the mixture of unsaturated fatty acids.

B. Bromination.—One and one-half grams of the unsaturated fatty acids was brominated,[11] yielding a white precipitate in the cold anhydrous ether. After washing with cold anhydrous ether and drying, the white brominated derivative gave a melting point of 175–176°.

The cold ether solution after the removal of free bromine was evaporated and the residue refluxed with hot petroleum ether. A white solid, insoluble in the hot petroleum ether, was filtered off, washed and dried. It gave a melting point of 170–172°. This solid was mixed with the precipitate obtained in the bromination above, extracted with hot petroleum ether and the petroleum ether extract combined with the same solution above. The residue of this extraction gave a melting point of 180–181°.

Anal. (Carius). Calcd. for hexabromostearic acid, $C_{18}H_{30}O_2Br_6$: Br, 63.34. Found: Br, 63.25.

These data indicate the presence of linolenic acid in the unsaturated fatty acids. It is interesting to note the detection of this acid as its bromide and the failure to find it as the oxidized product, hexahydroxystearic acid. This apparently shows that bromination is a more delicate method for detecting linolenic acid than oxidation.

When the petroleum ether from the above cooled, white crystals deposited. These were filtered off, redissolved in hot petroleum ether, allowed to crystallize and filtered. The white crystals obtained gave a melting point of 113–114°.

Anal. (Carius). Calcd. for tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$: Br, 53.33. Found: Br, 53.23.

These results are additional evidence of the presence of linolic acid in the unsaturated fatty acids.

Examination for Other Substances.—The result of a sodium fusion on the mixed fatty acids showed the absence of nitrogen, sulfur and halogens. A fusion of another sample of the mixed fatty acids with a mixture of equal parts of sodium carbonate and sodium nitrate showed the absence of phosphorus.

During the alcoholic saponification of the mixed fatty acids necessary in the preparation of the magnesium soaps for the separation of unsaturated fatty acids from the saturated, no unsaponifiable matter was noticed. The Liebermann–Burchard test for phytosterol[12] was negative. The test with 1% alcoholic digitonin[13] was also negative.

The results show the presence of four fatty acids—palmitic, oleic, linolic and linolenic—and the probable absence of other substances in the fatty acid mixture obtained by extracting the solid material resulting from the acid hydrolysis of cassava starch.

---

[10] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Co., New York, 1913, 5th ed., Vol. I, p. 564.

[11] Ref. 10, p. 573.

[12] Ref. 10, p. 270.

[13] Ref. 10, p. 264.

Summary

The fatty acids liberated by the hydrolysis of cassava starch free from extraneous fatty material have been found to be palmitic, oleic, linolic and linolenic.

The detection of small amounts of linolenic acid in the presence of oleic and linolic acids by bromination is a more delicate method than by oxidation.

This is the first time that linolenic acid has been found in a starch.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

FURAN REACTIONS. I. THE PYROLYSIS OF FURAN

BY CHARLES D. HURD AND A. R. GOLDSBY

RECEIVED FEBRUARY 26, 1932 PUBLISHED JUNE 6, 1932

Two possibilities of pyrolysis suggest themselves in the pyrolysis of furan. Either it should yield difuryl, a change analogous to the transformation of benzene into diphenyl, or it should break into carbon monoxide and gaseous hydrocarbons. Since no difuryl was found, the C–H union must be stronger than the C–O bond. Actually, the products formed were carbon monoxide and hydrocarbons. Because of the high temperature required (about 700°) it is interesting that methylacetylene was identified and that evidence was also obtained for cyclopropene: $C_4H_4O \longrightarrow CO + C_3H_4$. In addition, acetylene, ethylene, propylene, methane and butadiene were identified.

Preliminary work[1] in this Laboratory demonstrated the stability of furan at 600° if the hot contact time was less than one second. This is higher than the value of 450–490° reported by Sinkinson[2] as the "initial conducting temperature." It may be noted[3] that with a nickel catalyst (nickel on pumice, the oxide being reduced in a hydrogen stream at 280°) furan started to decompose at 360° when the contact time was thirteen to twenty seconds.

Furan was forced by displacement with mercury into an unpacked quartz tube (43 × 2 cm.) which was heated electrically for 32 cm. of its length. Within the tube was a glass-encased thermocouple. To condense the vapors, two empty flasks, cooled to −15°, were connected to the exit end of the tube, following which was a condensing coil at −80°.

Using 31–33 g. samples of furan it was found that by changing the duration of the experiment from 405 minutes to 110 minutes (a change of 59 to 15.6 sec. contact time) the percentage decomposition at 670–680°

[1] With F. D. Pilgrim.

[2] Sinkinson, *Ind. Eng. Chem.*, **17**, 31 (1925).

[3] From results obtained with John W. Garrett.

dropped from 41 to 12%. Similarly, at 740°, a change from 154 to 20 minutes (19.4 to 2.59 sec. contact time) diminished the decomposition from 74 to 17%. In the last two cases, the volumes of gas produced, respectively, were 9.3 and 1.5 liters.

In the 670° experiments, the gas was approximately three-fourths carbon monoxide, one-eighth saturated hydrocarbons and hydrogen, one-eighth unsaturated hydrocarbons. In the 740° experiments, analysis showed less carbon monoxide and more saturated hydrocarbons and hydrogen.

The Unsaturated Hydrocarbons.—The 11% of unsaturated hydrocarbons in the off-gas of the 740° and 2.59 sec. experiment was composed[4] of 3.1% acetylenes, 5.5% ethylene and 2.4% propylene admixed with undetermined amounts of allene, cyclopropene and butadiene. Longer contact times lowered the acetylene content but did not influence materially the others. That the acetylene content was largely methylacetylene was proved by liquefaction at −80° and conversion to dipropinylmercury, $(CH_3C{\equiv}C)_2Hg$, with alkaline potassium iodomercurate. With one crystallization from alcohol this derivative[5] melted at 196–204°. A small amount of acetylene resisted liquefaction. It gave the characteristic dull red cuprous derivative, Cu_2C_2.

Since methylacetylene is known[6] to pyrolyze into allene and since barium furoate has been reported[7] to yield cyclopropene, it is reasonably certain that both of these C_3H_4 gases were present. There is good evidence from an analogous study of furfural that butadiene was probably present also.

Benzene was definitely identified (as *m*-dinitrobenzene) in the liquid products of the reaction. Only 0.2 cc. of it was found in the experiment at 670° and 59 seconds, but 1.3 cc. was found in the experiment at 740° and 19.4 seconds. These aromatic liquids are traceable as secondary products through the unsaturated hydrocarbons mentioned above.

Summary

Furan decomposes at 670–740° in a quartz tube as contrasted with a temperature of 360° when heated in the presence of catalytic nickel. The pyrolysis proceeds by rupturing the nucleus into gaseous products. A condensation reaction leading to difuryl was not observed.

EVANSTON, ILLINOIS

[4] Analysis by method of Hurd and Spence, THIS JOURNAL, **51**, 3357 (1929).

[5] Johnson and McEwen, *ibid.*, **48**, 469 (1926).

[6] Hurd and Meinert, *ibid.*, **52**, 4543 (1930).

[7] Freundler, *Compt. rend.*, **124**, 1157 (1897); *Bull. soc. chim.*, [3] **17**, 613 (1897).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

FURAN REACTIONS. II. FURAN FROM FURFURAL

BY CHARLES D. HURD, A. R. GOLDSBY AND E. N. OSBORNE[1]

RECEIVED FEBRUARY 26, 1932 PUBLISHED JUNE 6, 1932

The present method[2] for making furan from furfural involves two steps: namely, a Cannizzaro oxidation of furfural to furoic acid, followed by thermal decarboxylation of the acid. In searching for a method which would give furan directly from furfural, two reactions were studied. One of these, which was very successful, consisted in allowing furfural to react with hot alkali. Furan was also formed in the pyrolysis of furfural, but the yields were less satisfactory than in the first reaction.

Furan from Furfural by Hot Alkali.—Fused alkali is an oxidizing agent capable of converting aldehydes into acids (as salts). Thus, acetaldehyde[3] gives rise to sodium acetate. With salts it is also a decarboxylating agent and it is pertinent that Limpricht[4] first prepared furan by heating barium furoate with soda lime. In the present investigation, excellent yields of furan were realized by dry-distilling an intimate mixture of sodium furoate and sodium hydroxide.

To ascertain if these two effects might be combined in the case of furfural in accordance with the equations

$$C_4H_3OCHO + NaOH \longrightarrow C_4H_3OCOONa + H_2$$
$$C_4H_3OCOONa + NaOH \longrightarrow C_4H_4O + Na_2CO_3$$

the behavior of fused sodium hydroxide and hot soda lime on furfural was investigated. Using this plan, excellent yields of furan were realized.

The flow method seemed to be the better of the two plans tried. In it, furfural vapors were passed through a hot iron pipe which was packed with soda lime. With a rapid flow, furan was isolated in yields as high as 86% of the theoretical. With the other method, furfural was dropped onto a molten mixture of sodium and potassium hydroxides. Yields of about 60% of furan were obtained. Encrustation of the surface of the molten alkali, due to carbonate formation, introduced difficulties which were not encountered in the flow method. Considerable quantities of carbon monoxide and traces of methylacetylene (or acetylene) accompanied the hydrogen in the gas. That these were secondary products of decomposition was established since they were also formed when furan (not furfural) was dropped on the fused alkali.

Pyrolysis of Furfural.—At high temperatures benzaldehyde breaks

[1] Holder of a Quaker Oats Fellowship, 1929–1930, administered through the Miner Laboratories, Chicago.

[2] Wilson, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 40.

[3] Fry and Schulze, THIS JOURNAL, **48**, 958 (1926).

[4] Limpricht, *Ann.*, **165**, 281 (1873).

down chiefly into carbon monoxide and benzene.[5] With a similar type of pyrolysis, furfural should yield carbon monoxide and furan. Preliminary work[6] demonstrated that no gases were formed as furfural was heated for three hours in a sealed tube at 200 or 275°. Most of the furfural was recoverable, leaving only a small amount of tarry residue on distillation. Using a flow method, 565° was found to be the initial decomposition temperature for a contact time of twenty seconds. With a reduced nickel catalyst, the decomposition temperature was lowered to 345°, which is somewhat higher than the temperature reported by Padoa and Ponti.[7] However, their catalyst may have been different and their contact time may have been longer.

With the flow method, furfural was found to give fair yields of furan. With a contact time of 0.2 second, only one-twentieth of the furfural decomposed at 660° and one-half at 900°. By increasing the contact time to four or five seconds, two-fifths of it decomposed at 725° whereas four-fifths was altered at 800° and three seconds. At 555° and sixty seconds furfural was found to decompose somewhat but over four-fifths of it was recoverable. The best conditions for furan production by pyrolysis were found to be 725° and a contact time of about five seconds. This gave a 16.5% yield.

Experimental Part

Furfural and Hot Alkali

Fused Alkali.—An iron flask about 30 cm. tall was improvised from a small gas-storage cylinder by removing the connections and drilling away the threads so as to leave a smooth hole in the top. A rubber stopper, bearing a reflux condenser tilted at an angle of 45°, was fitted into this hole. In the top of the condenser was a 2-holed rubber stopper which carried a dropping funnel the stem of which was drawn out to a capillary tip and a tube leading to another condenser which was directed downward for condensation. The first condenser was filled with hot water (about 75°) so as to let the furan escape but to return the furfural. The second condenser, which was cooled with tap water, was connected to a helical lead pipe which was surrounded by a freezing mixture of ice and salt. The condensed furan dropped into a cooled flask. The uncondensed furan was scrubbed out of the escaping gas by conducting it through four bottles (in series) of furfural (50 cc. each), all immersed in a freezing mixture at −20°.

Two moles of furfural were placed in the dropping funnel. In the iron flask were placed two moles of technical sodium hydroxide and two of potassium hydroxide. The furfural was added at the rate of about 0.4 g. per minute after the temperature of the salt-bath surrounding the iron flask reached 300°. Eight hours was taken for the addition. Gas evolution continued for about thirty minutes after all the furfural was introduced.

Of the 192 g. of furfural which was taken, 164 g. was decomposed since 28 g. was recovered. The liquid which distilled below 40° on the first fractionation was considered to be furan. It weighed 67.5 g., which was a 59% yield based on the decomposed furfural.

[5] Hurd and Bennett, THIS JOURNAL, **51**, 1197 (1929).

[6] With John W. Garrett.

[7] Padoa and Ponti, *Atti accad. Lincei*, [2] **15**, 610 (1906).

Several different modifications were tried without material benefit. The yields ranged from 54 to 64%. When the flask was heated by a direct flame considerable carbonization ensued although the yield of furan did not suffer. Curiously, only about 25–30% yields of furan were obtainable if the furfural which had been used for scrubbing was used directly on the hot alkali. One hundred cc. of this "scrubbing" furfural was found to contain 8 g. of water, 79 g. of furfural and 8 g. of a tarry residue. After redistillation this furfural again gave furan satisfactorily.

Other Products of the Reaction.—In a similar experiment wherein 29.0 g. of furfural was treated with 23.2 g. of fused sodium hydroxide, 19.7 g. of furfural was recovered. The 9.3 g. (0.097 mole) of furfural which underwent decomposition gave rise to 4.2 g. of furan (a 56% yield), 905 cc. of gas, and a carbonate residue. The gas was 71% hydrogen (0.029 mole), 22.2% carbon monoxide (0.009 mole), 4.2% methylacetylene or acetylene (0.0017 mole), and 2% carbon dioxide. The carbonate residue on acidification gave 1618 cc. of carbon dioxide. The carbonates in the original alkali gave but 20 cc. of carbon dioxide, hence 1598 cc. was generated in the reaction.

Similarly, when 9.44 g. of furan was dropped onto 10.2 g. of the fused alkali, 6.94 g. of furan was recovered and 137 cc. of gas was collected. *Anal.* CO, 67.14% or 0.0041 mole; H_2, 24.83, 0.0015; acetylenes, 7.94, 0.0005.

The gas formed when a mixture of 13.5 g. of sodium furoate and 4.0 g. of sodium hydroxide was dry distilled at 350–360° was similar. In all, 178 cc. was collected. It analyzed as follows (per cent. and mole): CO, 65.17, 0.0052; H_2, 26.42, 0.0021; acetylenes, 8.37, 0.0007. The yield of furan in this experiment was 6.2 g. or 92.6%.

Flow Method with Soda Lime.—Furfural (760 g.) was distilled during three hours into an iron pipe, 120 × 5 cm., which was about half filled with soda lime. Rubber stoppers were used for the connections. The pipe was heated for about half of its length and an inside temperature of 350–360° was maintained, as shown by a thermometer inside the pipe.

Furfural and furan were condensed from the effluent gas as previously described and the uncondensed gas was stored in a gasometer. On working up the products, 696 g. of furfural was recovered and 39 g. of furan formed, a yield which is 86% of the theoretical.

In a similar experiment wherein 600 g. of furfural was admitted during twelve hours (thus, a slower rate of flow), 318 g. was recovered and 94.5 g. of furan was formed. Here the percentage yield is only 47.5.

A 63% yield (18.5 g.) of furan was realized at 450° (a thermocouple used for the inside temperature) by distilling 192 g. (151 g. recovered) of furfural during three hours through a Pyrex tube which contained a charge of soda lime.

Pyrolysis of Furfural

Apparatus.—The apparatus used was similar to the one described for the pyrolysis of furan, furfural being introduced by displacement with mercury (see preceding paper). The 2-cm. quartz tube was used in most of the experiments but a tube of 0.55 cm. bore was used for the experiments with contact times of less than one second. Furfural and some furan was condensed from the effluent gas by cooling it to −15°. The remaining furan was removed either by cooling in a coil at −80° or by scrubbing with furfural at −15°. The effluent gas was metered and stored over salt solution in a gasometer. The essential data for six characteristic runs are given in Table I.

Gas.—The gas from each run was analyzed, a typical case showing 80% carbon monoxide, 3% carbon dioxide, 6.5% unsaturated hydrocarbons, 10% hydrogen plus saturated hydrocarbons. Generally, about one-fifth of the unsaturated hydrocarbons was ethylene; two-fifths was a mixture of methylacetylene and acetylene, chiefly the former; the remaining two-fifths was absorbed in 82.4% sulfuric acid and was a mixture

TABLE I

DATA FOR THE PYROLYSIS OF FURFURAL

Furfural taken, g.....	88.5	115	115	259	805	115
Furfural decomposed, g....	83.5	46	26.5	142.5	658	63.5
Extent of decompn., %...	94	40	23	55	82	55
Temperature, °C.....	680	725	755	780	800	900
Duration of expt., min....	112	93	100	184	425	60
Contact time, seconds.....	19.4	4.9	0.40	4.0	2.9	0.21
Gas formed (0°), liters....	36.2	24.3	11.5	112	308	....
Benzene isolated, g.....	2.6	0.9	0.4	...	19	0.2
Toluene isolated, g.....	2.5	...	...	...	5.5	....
Carbon formed, g.....	...	...	...	...	17	....
Furan yield, g.....	2.0	5.4	2.0	8.2	22	0.2
Furan yield, %.....	3.4	16.5	10.0	8.1	4.7	0.4

of propylene, allene, butadiene and cyclopropene. The methylacetylene was established through the mercury derivative, $(CH_3C{\equiv}C)_2Hg$.

In several runs, the unsaturated content of the gas was converted into bromide derivatives. The dibromide fraction was found by refractive index measurements to be a mixture of about equal weights of ethylene and propylene bromides. For each cc. of dibromides there was produced about 1.5 cc. of tetrabromides. From the latter, butadiene tetrabromide, m. p. 116–116.5°, separated easily. Its identity was confirmed by a mixed melting point determination with an authentic specimen prepared from phosphorus pentabromide and erythritol. In the experiment wherein 805 g. of furfural was taken, 11 g. of pure butadiene tetrabromide was secured and, of course, more was held in the mother liquor. The latter contained tetrabromides of methylacetylene, acetylene, allene and cyclopropene. This material evolved hydrogen bromide[8] at room temperature.

The mixture of tetrabromides from which the butadiene tetrabromide had been filtered off was added dropwise on zinc dust and boiling alcohol. Analysis of the unsaturated hydrocarbons which were thus regenerated showed the presence of 20% acetylenes and 80% other gases which were soluble in 82% sulfuric acid. The latter points to allene, cyclopropene or butadiene inasmuch as propylene should have been largely eliminated.

Liquid Products.—Furan, benzene and toluene were separated from the liquid products by distillation. Yields of 13–16.5% of furan were realized at 725° and about five seconds contact time. Higher temperatures, even with a diminished contact time, lessened the yield.

The benzene fraction was characterized by converting it into *m*-dinitrobenzene, m. p. 89°. In the 105–115° fraction, toluene was identified as 2,4-dinitrotoluene, m. p. 69–70°.

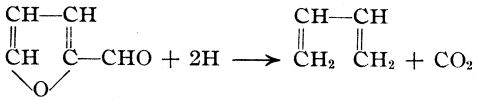
After distillation of the unused furfural, considerable residue boiling above 185° remained. This was largely phenolic. From the 88.5 g. (of furfural) run at 680° and 19.4 sec., 15 g. of this residue was encountered. Eleven grams of this was extracted with 10% sodium hydroxide solution whereupon 6 g. of phenolic material was obtained. Another 3 g. of similar material was extracted from the residue by refluxing for half an hour with 50 cc. of 20% sodium hydroxide solution. This material was not soluble in sodium bicarbonate solution. Hence, it could not have been furoic acid and, therefore, furfuryl furoate could not have been present in the original mixture. It will be recalled that under certain conditions of pyrolysis benzaldehyde changes into benzyl benzoate.

[8] Freundler, *Compt. rend.*, **124**, 1157 (1897), reported that cyclopropene tetrabromide behaved in this way.

The tarry material which was not soluble in alkali would have contained any difuryl. α,α'-Difuryl is reported[9] to distil at 240° and 7 mm. Our residue gave no distillate in this range.

Distillation of the phenolic portion gave a fraction, b. p. 183–190°. This was identified as phenol, for it yielded pure tribromophenol readily with bromine. An unidentified phenolic fraction was collected between 205–245° but the 245–250° fraction solidified on cooling. The latter melted at 46°, which suggests 2,6-dimethylphenol, m. p. 49°. The α-naphthyl isocyanate derivative[10] of this phenol is not listed, but the higher melting 2,5-dimethylphenol gives a derivative melting at 172–173°. Our 46° material gave a derivative which melted at 174–175°. Molecular weight evidence on the 46° material was satisfactory for a xylenol. Trinitrotoluene was used as a cryoscopic solvent[11] and to test the method cresol gave a value of 104.5 as compared with the theoretical value of 108. The 46° crystals gave a value of 115, whereas the mol. wt. of xylenol is 122.

Dilution Experiment with Hydrogen.—No carbon dioxide was formed in the pyrolysis of furan (see preceding paper) but with furfural it comprised 2 to 3% of the gas. Since its formation was approximately equivalent to that of butadiene, it suggested the following equation



Accordingly, it was of interest to study the effect of hydrogen on furfural at high temperatures. The results showed a minor increase in the total unsaturated gases but in general no marked change resulted. For example, using a temperature of 750°, 245 g. of furfural was passed through the furnace in 218 minutes together with a current of dry hydrogen, introduced at a rate of 50–300 cc. per minute. There were formed 6 g. of furan, 4 g. of benzene and 3.5 g. of butadiene tetrabromide. The other liquid and gaseous products were also similar to those obtained without the admixed hydrogen.

Summary

Toward heat alone, furfural changes above 550° into furan and its decomposition products, carbon monoxide, methylacetylene, etc. Also, butadiene, benzene, toluene, phenol and a xylenol were identified. Excellent yields of furan were realized by passing furfural vapors through soda lime at 350° or through fused sodium hydroxide. Hydrogen was liberated and the hydroxide was changed to carbonate. The hot alkali converted a small portion of the furan into gaseous products.

EVANSTON, ILLINOIS

[9] Kondo and Suzuki, *J. Pharm. Soc. Japan*, No. **544**, 501 (1927).

[10] French and Wirtel, THIS JOURNAL, **48**, 1736 (1926).

[11] Pastak, *Bull. soc. chim.*, **39**, 82 (1926).

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TOXICAROL. IV. CONCERNING THE STRUCTURE OF TOXICAROL

BY E. P. CLARK

RECEIVED MARCH 16, 1932 PUBLISHED JUNE 6, 1932

Toxicarol when refluxed with 5% alcoholic potassium hydroxide solution loses the elements C_5H_6 and yields a colorless phenolic substance, $C_{18}H_{16}O_7$. This new compound, which has been named apotoxicarol, has the following properties. It contains a grouping having two hydrogen atoms that are readily removed by gentle oxidation, forming a dehydro derivative, $C_{18}H_{14}O_7$. It contains no readily reducible double bond; it has one more phenolic hydroxyl group than its precursor, toxicarol; and, upon oxidation with alkaline hydrogen peroxide, two acids are obtained, the structure of which can be deduced from facts now available.

The experimental evidence upon which the foregoing statements are based is as follows. When oxidized with iodine in hot alcoholic potassium acetate solution, apotoxicarol formed an iodo compound which, when treated with zinc dust and boiling acetic acid, was readily dehalogenated, forming dehydroapotoxicarol, $C_{18}H_{14}O_7$. The transformation is exactly analogous to the one which occurs when toxicarol is similarly treated[1] and indicates that the grouping responsible for the change is the same in both substances.

The readily reducible double bond present in toxicarol is absent in apotoxicarol, as shown by the latter's failure to absorb hydrogen when treated with this reagent in the presence of an active platinum catalyst.

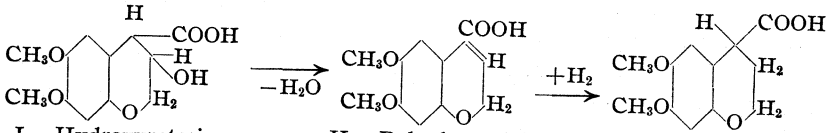
It has been shown that acetylation of toxicarol with boiling acetic anhydride and sodium acetate yields a diacetyl derivative,[1] but methylation, irrespective of the methods employed, has consistently given negative results. Apotoxicarol, however, when subjected to acetylation and methylation, as employed for toxicarol, gave, respectively, a triacetyl derivative and a monomethyl ether. It thus follows that the reaction involved in the formation of apotoxicarol consists of the loss from toxicarol of the elements C_5H_6, and the generation of a new hydroxyl group. It also shows that the double bond existing in toxicarol is undoubtedly associated with the grouping eliminated. These facts may be explained in several ways, but because there is not yet sufficient evidence available on which to base a decision, no interpretation of the reaction will be made at this time.

The oxidation of apotoxicarol with alkaline hydrogen peroxide, however, has yielded products which materially clarify the problem of the structure of toxicarol.

[1] Clark, THIS JOURNAL, **53**, 2264 (1931).

When apotoxicarol dissolved in aqueous alkali was treated with hydrogen peroxide, a vigorous reaction occurred, and two monocarboxylic acids were formed. One was a colorless substance whose molecular composition was $C_{12}H_{14}O_6$. The second acid was a brownish-yellow crystalline material, $C_{12}H_{12}O_5$. It was possible by regulating the conditions of the reaction to obtain dominantly either one or the other substance; furthermore, the first acid could be readily converted to the second by treatment with acetic anhydride.

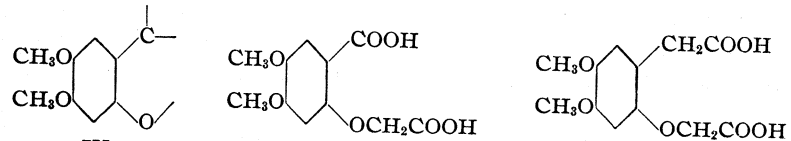
The second acid, $C_{12}H_{12}O_5$, contained a double bond which was readily reduced, and the dihydro derivative thus formed was shown by comparison with an authentic sample to be netoric acid.[2] The yellow acid, $C_{12}H_{12}O_5$, was therefore dehydronetoric acid, whereas the white acid, $C_{12}H_{14}O_6$, was hydroxynetoric acid. The structure of netoric acid has not been determined, but evidence now available indicates that, as LaForge, Haller and Smith[3] have already suggested, it may be represented by III. Dehydro- and hydroxynetoric acid would then be represented, respectively, by II and I.



I. Hydroxynetoric acid, $C_{12}H_{14}O_6$ II. Dehydronetoric acid, $C_{12}H_{12}O_5$ III. Netoric acid, $C_{12}H_{14}O_5$

The reasoning involved in these statements is as follows. It has been shown in the third communication of this series[4] that permanganate oxidation of dehydrotoxicarol yields 2-hydroxy-4,5-dimethoxybenzoic acid and risic acid (V), which is 2-carboxy-4,5-dimethoxyphenoxyacetic acid. It was also shown that treatment of dehydrotoxicarol with alcoholic alkali yields a non-crystallizable acidic material probably consisting essentially of a compound analogous to derrisic and deguelic acids.

This acidic material when oxidized with aqueous permanganate also yields risic acid, but if it is oxidized with alkaline hydrogen peroxide, derric acid (2-carboxymethyl-4,5-dimethoxyphenoxyacetic acid, VI) is formed. These reactions prove that in the methoxylated portion of dehydrotoxicarol the grouping IV exists.



IV V. Risic acid VI. Derric acid

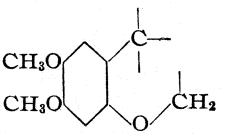
[2] Smith and LaForge, THIS JOURNAL, **52**, 4595 (1930).

[3] LaForge, Haller and Smith, *ibid.*, **53**, 4402 (1931).

[4] Clark, *ibid.*, **54**, 1600 (1932).

It is now evident that the methylene group in the —O—CH_2COOH complex in risic acid (V) must have existed as such in dehydrotoxicarol, for there is no conceivable reaction whereby permanganate oxidation could cause two hydrogen atoms to be added to or exchanged for other substituents upon the carbon atom under discussion. It will also be shown later that the —O—CH_2 portion of the oxyacetic acid radical in derric acid (VI) was likewise present in dehydrotoxicarol.

From what has just been presented it follows that in dehydrotoxicarol there exists the atomic grouping VII consisting of $C_{10}H_{10}O_3$. The difference between this formula and that of netoric acid, $C_{12}H_{14}O_5$, after deducting a carboxyl group, is CH_3. This must of necessity form a saturated ring, and the conclusion therefore emerges that netoric acid is represented by III or by the isomeric form in which the carboxyl group is attached to the carbon atom β to the oxygen of the pyran ring.

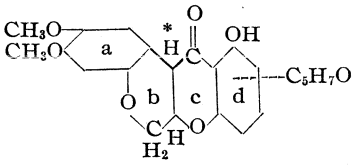


VII

That formula I is undoubtedly the correct interpretation follows from facts previously published together with some new observations which will now be considered.

All direct attempts to prove the presence of a carbonyl group in toxicarol by securing characteristic derivatives such as oximes or semicarbazones have failed, but evidence of a different character definitely indicates the presence of a carbonyl group in toxicarol. The facts to be considered in this connection also indicate that the phenolic hydroxyl group in toxicarol is ortho to the carbonyl group and that one of the hydrogen atoms which is readily removed by mild oxidation in the dehydro formation is attached to a carbon atom adjacent to the carbonyl group.

In order conveniently to present the evidence in support of the statements just made, a formula which is provisionally submitted as representing the structure of toxicarol (VIII) will be used.



VIII. Toxicarol

Previously recorded information concerning the acyl derivatives of toxicarol[1] is as follows. Toxicarol when treated with benzoyl chloride in pyridine forms a monobenzoyl derivative; but when it is acetylated with acetic anhydride and sodium acetate, a diacetate is obtained. The diacetate is more reactive toward oxidizing agents than is toxicarol, and it is capable of reduction to monoacetyldihydrodesoxytoxicarol.

These data when considered together with other reactions to be subsequently discussed may be explained on the basis of a keto–enol mechanism.

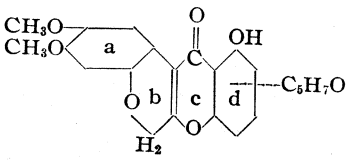
Benzoylation of toxicarol in the manner in which the reaction was conducted affected only the hydroxyl group on the benzene ring *d;* but

acetylation with boiling acetic anhydride and sodium acetate caused the acetylation not only of the phenolic hydroxyl group but also of the enol formed by the migration of the hydrogen marked with the asterisk to the carbonyl group. Reduction of the enol-acetate to monoacetyldihydrodesoxytoxicarol is in harmony with the results recently recorded by Roll and Adams[5] in which they show that enol-acetates are reduced to desoxy compounds with the elimination of the acetoxyl group. According to the mechanism here proposed, diacetyltoxicarol would be an enol compound with a double bond in ring *c* and consequently would be more susceptible to oxidation than would toxicarol.

In order to supplement these deductions the results obtained by hydrolyzing diacetyltoxicarol are also presented. When rapidly hydrolyzed with sodium methylate, a product was obtained differing from toxicarol in crystalline habit and in having a lower melting point (160–170°). Upon several rapid recrystallizations of this material, the low-melting rods changed to plates whose melting point was 220°, which is characteristic of toxicarol. This phenomenon may be accounted for by the fact that an enol form of toxicarol is liberated which upon recrystallization reverts to the keto form.

Dehydrotoxicarol is characterized by its ability to enter into reactions which yield the several acids mentioned before, and forms only one acetyl derivative. It undergoes the Dakin reaction[6] when treated with alkaline hydrogen peroxide, in which process the linkage between the carbonyl group and the benzene ring to which it is attached is split, with the formation of carboxyl and a new phenolic hydroxyl group.

These reactions become intelligible if the formation of dehydrotoxicarol is explained by the elimination of the two hydrogen atoms attached to the carbon atoms common to the two pyran rings. The removal of these two hydrogen atoms generates a double bond between the carbon atoms under discussion so that dehydrotoxicarol would be represented by IX.



IX. Dehydrotoxicarol

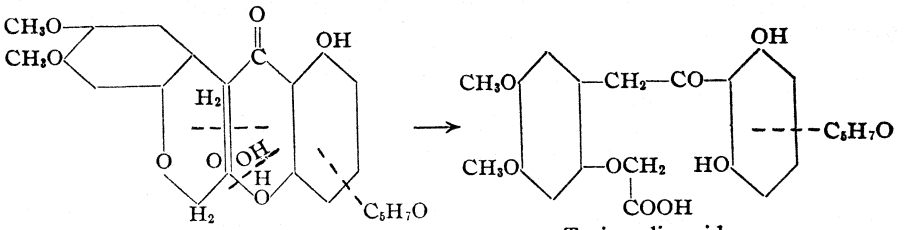
A compound of this structure would be expected to undergo the reactions given as characteristic of dehydrotoxicarol. For example, in considering the methoxylated portion of the molecule, it would be anticipated that permanganate would attack the double bond first, forming a diol which, as the reaction proceeded, would be further oxidized to risic and then to 2-hydroxy-4,5-dimethoxybenzoic acid. The two latter products, as stated before, are invariably formed when dehydrotoxicarol is treated with permanganate. Dehydrotoxicarol, according to the structure postu-

[5] Roll and Adams, THIS JOURNAL, **53**, 3469 (1931).

[6] Dakin, *Am. Chem. J.*, **42**, 477 (1909).

lated for it, no longer contains a hydrogen atom capable of migrating to the carbonyl oxygen to form an enol. Consequently it is only possible, as found experimentally, to form a monoacetyl derivative.

The splitting of dehydrotoxicarol with alcoholic alkali to form an acid analogous to derrisic and deguelic acids may also be explained on the basis of the structure represented by IX. This reaction is in all probability a simple hydrolysis which occurs at a double bond adjacent to a carbonyl group.[7] It may be represented thus



Dehydrotoxicarol Toxicarolic acid

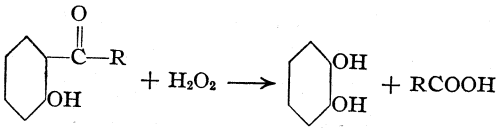
As pointed out before, no crystalline material corresponding to toxicarolic acid has been obtained, doubtless due to the lability toward alkali of the C_5H_7O group. However, when dehydrodihydrotoxicarol[1] was treated with alcoholic alkali, there was obtained in very good yield a crystalline monocarboxylic acid which analyzed for dihydrotoxicarolic acid. When treated with boiling acetic anhydride, this acid underwent a reaction which was the reverse of that by which it was formed, yielding a monoacetyl dehydrodihydrotoxicarol. This process is analogous to the way in which derrisic and deguelic acids, respectively, revert to dehydrorotenone and dehydrodeguelin. It was possible, however, to block the condensation by esterifying the carboxyl group. When this was done and the hydroxyl groups were acetylated with acetic anhydride and pyridine, a diacetyldihydrotoxicarolic acid ester was produced, showing that in the formation of the acid a new phenolic hydroxyl group was developed which, according to the equation given above, was due to the breaking of the oxygen bridge in ring *c*. This reaction is exactly analogous to the one which occurs with dehydrorotenone[8] and dehydrodeguelin.[9]

The Dakin reaction to which previous reference has been made is of unusual importance when applied to dehydrotoxicarol and its derivatives. It may be described as the oxidation of ortho- and para-hydroxy derivatives of benzaldehyde, acetophenone and related substances to polyphenolic compounds and an acid. The reaction may be illustrated by the equation

[7] Houben, "Die Methoden der org. Chem.," III auf., 1925, p. 1021.

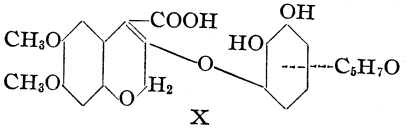
[8] Butenandt, *Ann.*, **464**, 272 (1928).

[9] Clark, THIS JOURNAL, **53**, 2369 (1931).



The formation of derric acid by alkaline hydrogen peroxide oxidation of toxicarolic and dihydrotoxicarolic acids, when considered in relation to the reaction above, furnishes more direct evidence that the structures assigned the last-named acids are probably correct.

When the same reaction was applied to dehydrotoxicarol a similar split occurred at the carbonyl group and gave an acid, $C_{23}H_{22}O_9$ (X).



X

This material has been designated as dehydrotoxicarol monocarboxylic acid. In the formation of this material, according to the Dakin reaction, the oxygen linkage of ring *c* remained intact, thus forming an ether. The compound was hydrogenated to a dihydro derivative, indicating that the double bond adjacent to the carboxyl group was not affected. In support of this contention an excess of hydrogen peroxide in a boiling strongly alkaline solution oxidized the ether to risic acid.

When the monocarboxylic acid was acetylated by the method of Chattaway,[10] only a monoacetyl derivative was formed, whereas a diacetate was to be expected. Attempts to obtain a diacetyl compound by more drastic methods of acetylation only resulted in material which would not crystallize. However, the presence of a free hydroxyl group in the monoacetyl derivative was indicated by a faint ferric chloride test.

The formation of dehydrotoxicarol monocarboxylic acid by means of the Dakin reaction is significant as it shows that the phenolic hydroxyl group in ring *d* of dehydrotoxicarol and consequently of toxicarol is either ortho or para to the carbonyl group. However, the results relative to the failure to methylate toxicarol, reported earlier in this discussion, are sufficient proof that the position of the OH group is ortho to the carbonyl, for it is well known that an hydroxyl ortho to an carbonyl group is refractory to methylation.[11]

It follows from what has preceded that apotoxicarol may be represented by VIII with the C_5H_7O group replaced by an hydroxyl. From this structure it is possible to decide which of the two configurations proposed for netoric acid (III) is correct. The Dakin reaction applied to apotoxicarol

[10] Chattaway, *J. Chem. Soc.*, 2495 (1931).

[11] Gomm and Nierenstein, THIS JOURNAL, **53**, 4408 (1931), and references quoted therein.

should cause ring *c* to be split, converting the carbonyl group to a carboxyl group. With the substituents on ring *d* differing from those in toxicarol, the reaction proceeds with the elimination of ring *d* in such a manner that the oxygen atom in ring *c* forms an hydroxyl group on the carbon atom ortho to the methylene group of ring *b*. Thus hydroxynetoric acid (I) is formed, and this, as pointed out, loses the elements of water, forming dehydronetoric acid (II). The latter upon reduction yields netoric acid (III). It follows from this series of reactions that the position of the carboxyl group in netoric acid is as represented in III.

With the exception of optical activity, all available experimental data relative to the structure of toxicarol are in agreement with formula VIII. In this formula there are two optically active centers, namely, the carbon atoms common to rings *b* and *c*. In preparing toxicarol, however, it is necessary to treat with alkali the non-crystallizable extractives in which it is found and this process undoubtedly causes complete racemization. It would certainly occur at the carbon atom containing the hydrogen adjacent to the carbonyl group because alkali has been shown to cause a keto–enol change. No importance, therefore, is attached to the fact that toxicarol is optically inactive.

The reactions involved in the foregoing discussion which are presented for the first time are summarized in the accompanying chart.

Experimental

Apotoxicarol.—A mixture of 5 g. of toxicarol, 100 cc. of absolute alcohol and 10 cc. of a 50% aqueous potassium hydroxide solution was refluxed for three hours. The resulting liquid was then diluted with 1 liter of water and treated with 100 cc. of a 7.5% solution of calcium chloride. The resulting precipitate was removed by means of a folded filter, and the filtrate was acidified to Congo red with hydrochloric acid.

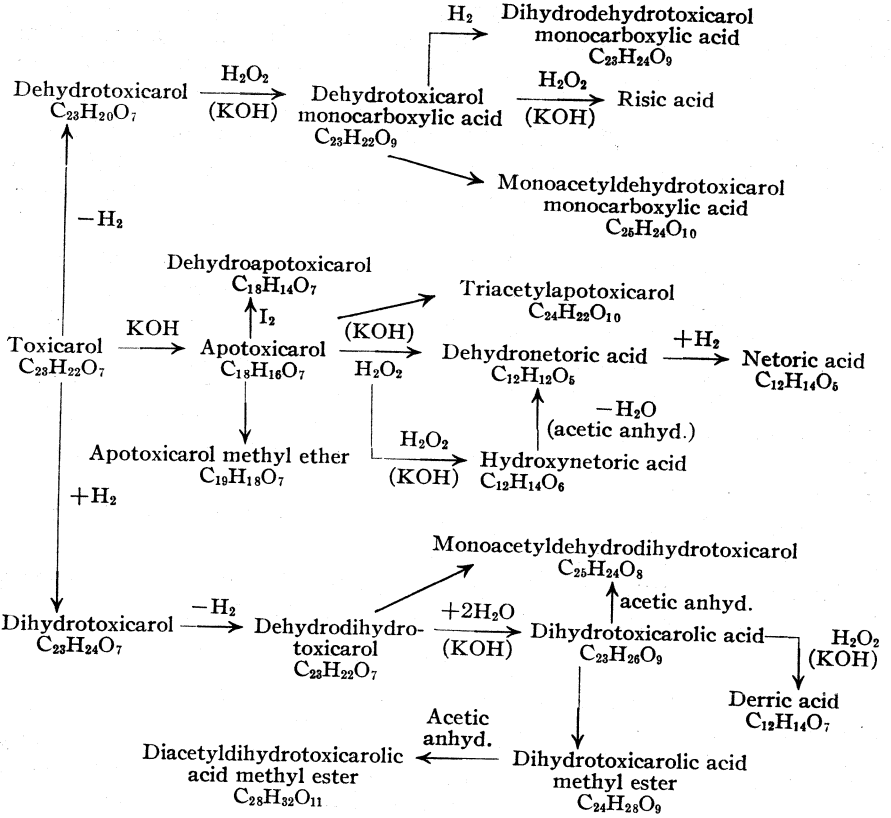
The flocky precipitate thus formed was allowed to settle, and the greater part of the supernatant solution was decanted. The remaining liquid with the precipitate was transferred to a separatory funnel and shaken with ether. The aqueous liquid was discarded, and the ether with the insoluble precipitate was shaken with fresh water, which in turn was discarded. The solid material suspended in the ether was collected upon a filter and dried.

It was purified by recrystallization from a hot saturated acetic acid solution by the addition of two volumes of methanol. The yield from 50 g. of toxicarol was usually 6 g. of crude material. Upon recrystallization this gave 4 g. of apotoxicarol whose melting point was 244°. For analysis it was recrystallized until it had a constant melting point of 246–247°. It consisted of small white rods, which frequently occurred in rosets, and it gave a deep reddish-violet color with ferric chloride.

Anal. Calcd. for $C_{18}H_{16}O_7$: C, 62.78; H, 4.69; OCH_3 (2), 18.1. Found: C, 62.91; H, 4.81; OCH_3, 18.3.

Dehydroapotoxicarol.—One gram of apotoxicarol and 1.5 g. of potassium acetate were dissolved in 50 cc. of absolute ethanol and treated portion-wise with 20 cc. of an absolute ethanolic solution of 1 g. of iodine. The reaction mixture was allowed to stand for a day, after which the yellow crystalline iodo compound (0.65 g.) was removed by filtration. The substance evolved iodine at approximately 200°, but it did not melt

NEW REACTIONS OF TOXICAROL AND SOME OF ITS DERIVATIVES



even when heated to 310°. When the iodo compound was boiled for one and one-half hours with 25 cc. of acetic acid and 1 g. of zinc dust, dehalogenation occurred, yielding 0.2 g. of dehydroapotoxicarol. When treated with water, the mother liquors from which the crystalline iodo compound was obtained gave an amorphous precipitate. This material after having been dried was treated with zinc dust and acetic acid as above, yielding 0.1 g. of dehydroapotoxicarol.

For analysis the dehydroapotoxicarol was crystallized from a hot phenol solution by adding two volumes of methanol. It separated as light greenish-yellow rods and needles, which upon heating gradually darkened and sintered and finally melted at 298°. In parallel polarized light (crossed nicols) the extinction was straight and the elongation was negative. The polarization colors were brilliant. No interference figures were observable in convergent polarized light (crossed nicols), but the substance appeared to be biaxial: η_α, 1.543 (lengthwise); η_β, 1.685 (crosswise); $\eta_\gamma > 1.740$ (crosswise). Some rods, however, matched a liquid of η 1.740; all ± 0.003.[12]

Anal. Calcd. for $C_{18}H_{14}O_7$: C, 63.15; H, 4.12; OCH_3 (2), 18.1. Found: C, 63.10; H, 4.28; OCH_3, 18.3.

[12] The optical data reported in this communication were determined by George L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture.

Triacetylapotoxicarol.—A mixture of 0.5 g. of apotoxicarol, 4 cc. of acetic anhydride and 0.1 g. of anhydrous sodium acetate was boiled for fifteen minutes. The condenser was then removed, and three-fourths of the anhydride was boiled away. When the residue was treated with water the acetyl compound became solid. The yield was 0.6 g. The crude material was purified by dissolving it in 15 cc. of hot acetic acid, filtering the solution through norit and then adding two volumes of methanol.

The pure acetyl compound (0.3 g.) separated as colorless square micaceous plates which melted at 206°. The plates extinguished sharply in parallel polarized light (crossed nicols), precluding satisfactory interference figures. However, the material appeared to be biaxial when examined in convergent polarized light (crossed nicols): η_α, 1.547 (common); η_β, indeterminate; $\eta_\gamma > 1.740$; an intermediate value η_i, 1.645 is commonly found; all ± 0.003.

Anal. Calcd. for $C_{24}H_{22}O_{10}$: C, 61.26; H, 4.72; OCH_3 (2), 13.2; acetyl, 27.5. Found: C, 61.38; H, 4.75; OCH_3, 13.4; acetyl, 27.8.

Apotoxicarol Methyl Ether.—One gram of apotoxicarol suspended in 10 cc. of hot methanol was dissolved by adding 10 cc. of a 10% methanolic potassium hydroxide solution. Two and five-tenths cc. of dimethyl sulfate was then added all at once, and after the reaction had subsided the mixture was again subjected to the same treatment with 10 cc. of potassium hydroxide solution and 2.5 cc. of dimethyl sulfate. The reaction was completed by boiling the mixture for five minutes, after which the product was separated by adding 10 volumes of water. Nine-tenths gram of crude material whose melting point was approximately 218° was obtained. The substance was recrystallized from a hot chloroform solution by adding two volumes of methanol. Purification by this procedure was repeated until the product had a constant melting point of 236–237°. It consisted of sheaves and rosets of fine colorless needles and gave a dark brownish color with ferric chloride. In parallel polarized light (crossed nicols) the extinction was inclined, and the elongation was negative. The crystals were apparently biaxial: η_α, 1.600; η_β, indeterminate; $\eta_\gamma > 1.740$ (both ± 0.003).

Anal. Calcd. for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06; OCH_3 (3), 26.0. Found: C, 63.75; H, 5.14; OCH_3, 25.8.

Hydroxynetoric Acid.—Two grams of apotoxicarol was dissolved in 35 cc. of 7.5% potassium hydroxide solution and treated portion-wise with 10 cc. of 30% hydrogen peroxide. A vigorous reaction occurred in which the color of the solution became first brown, then deep claret and finally a dark straw color. At the same time the liquid became boiling hot. After the reaction had subsided, the mixture was boiled for several minutes and then made acid to Congo red with sulfuric acid. Approximately 0.1 g. of dehydronetoric acid separated (see below). This was removed by filtration, and the filtrate was allowed to evaporate to dryness in the air. The residue was extracted with acetone, and the resulting solution was concentrated to a volume of 8 cc. Upon standing, 0.35 g. of hydroxynetoric acid separated. It was recrystallized from its solution in butyl ether, obtained by dissolving the acid in boiling acetone, adding two volumes of butyl ether and removing the acetone by distillation. The pure acid separated as colorless irregular-shaped plates, and occasionally rhomb-like forms, which melted at 189°. In parallel polarized light (crossed nicols) the plates extinguished sharply and showed second and third order polarization colors. In convergent polarized light (crossed nicols) the material appeared to be biaxial, although interference figures were rarely found: η_α, 1.513 (common); η_β, indeterminate; η_γ, 1.660 (both ± 0.003).

Anal. Calcd. for $C_{12}H_{14}O_6$: mol. wt., 254.2; C, 56.67; H, 5.57; OCH_3 (2), 24.4. Found: mol. wt. (titration), 258; C, 56.98; H, 5.66; OCH_3, 24.4.

Dehydronetoric Acid.—When 10% potassium hydroxide solution was used in the procedure described above for the preparation of hydroxynetoric acid, the reaction

gave exclusively dehydronetoric acid. This was obtained by acidifying the reaction mixture with sulfuric acid. The yields from experiments with 2 g. of apotoxicarol were variable, ranging from 0.35 to 0.8 g. The crude acid was purified by treating with norit an aqueous solution of the potassium salt acidified with acetic acid, after which the free acid was obtained by acidifying the filtrate with sulfuric acid.

The material had a brownish-yellow color and melted at 212° with decomposition. It consisted of short isodiametric prisms, longer rod-like prisms with square ends, and still more slender forms resembling needles. In parallel polarized light (crossed nicols) the extinction was straight and the elongation was negative. The material was biaxial, although in convergent polarized light (crossed nicols) interference figures were rarely found: η_α, 1.533 (commonly shown lengthwise on rods with square ends); η_β, 1.678 (very common on rods crosswise); $\eta_\gamma > 1.740$. Many rods, however, matched a liquid of η 1.740 (crosswise); all ± 0.003.

Anal. Calcd. for $C_{12}H_{12}O_5$: mol. wt., 236.2; C, 60.99; H, 5.12; OCH_3 (2), 26.27, Found: mol. wt. (titration), 233; C, 60.98; H, 5.17; OCH_3, 26.1.

Action of Acetic Anhydride upon Hydroxynetoric Acid.—Three-tenths gram of hydroxynetoric acid and 2 cc. of acetic anhydride were gently heated until the solution began to boil. The liquid was then allowed to cool for one minute, after which most of the solvent was removed by a rapid blast of air. Methanol was then cautiously added to decompose the remaining acetic anhydride, and the resulting solution was again evaporated with a current of air. When water was added to the residue, 0.25 g. of crude material was obtained, which, after recrystallization by the method given in the preceding paragraph, possessed all the properties recorded for dehydronetoric acid.

Reduction of Dehydronetoric Acid.—An ethyl acetate solution of 0.3 g. of dehydronetoric acid was reduced with hydrogen and the platinum catalyst of Voorhees and Adams.[13] The product obtained after removing the catalyst and solvent was dissolved in 5 cc. of boiling water and purified by filtration through norit. Upon cooling, the solution rapidly crystallized. The product contained water of crystallization, which was readily lost when the material was dried at 60° in a vacuum over potassium hydroxide. The dried acid melted sharply at 134°, and when mixed with an authentic sample of netoric acid, recrystallized in the same manner as the material under investigation, no depression of the melting point occurred. The reduction product was therefore netoric acid.

Dihydrotoxicarolic Acid.—A mixture of 5 g. of dehydrodihydrotoxicarol,[14] 5 g. of zinc dust, 120 cc. of ethanol and 30 cc. of 50% potassium hydroxide solution was refluxed for thirty minutes. The clear solution was then separated from the zinc, diluted to 500 cc. with water and ice and carefully acidified to Congo red with sulfuric acid. The precipitate which was formed rapidly crystallized, yielding 5.2 g. of material which melted between 110 and 120°. When a solution of the substance in hot methanol was diluted with an equal volume of hot water, the dihydrotoxicarolic acid separated as thin, frequently elongated, hexagonal plates which melted at 129° with the evolution of gas. It gave a purple color with ferric chloride. In parallel polarized light (crossed nicols) the extinction was straight and the elongation was negative. Double refraction was extremely strong. The plates usually extinguished sharply: η_α, 1.515 (common lengthwise on elongated plates); η_β, indeterminate; η_γ, 1.600 (common on elongated plates crosswise); both ± 0.003.

---

[13] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

[14] This compound may advantageously be made by oxidizing dihydrotoxicarol with iodine in potassium acetate solution in the manner recorded for the preparation of dehydrotoxicarol.[1] The yield is usually 75%.

Anal. Calcd. for $C_{23}H_{26}O_9$: mol. wt., 446.3; C, 61.87; H, 5.87; OCH_3 (2), 13.9. Found: mol. wt. (titration), 451; C, 61.54; H, 6.13; OCH_3, 14.0.

Monoacetyldehydrodihydrotoxicarol from Dihydrotoxicarolic Acid.—One gram of dihydrotoxicarolic acid, 4 cc. of acetic anhydride and 0.25 g. of anhydrous sodium acetate were refluxed for fifteen minutes. The condenser was then removed and most of the anhydride was boiled away, after which 10 cc. of methanol was added to the residue. Two-tenths gram of material separated which, after it was recrystallized by treating a chloroform solution of the substance with five volumes of methanol, melted at 238°. The material was shown to be monoacetyldehydrodihydrotoxicarol by comparison with a sample of this compound prepared by acetylating dehydrodihydrotoxicarol according to the procedure just given.

Dihydrotoxicarolic Acid Methyl Ester.—One gram of dihydrotoxicarolic acid was dissolved in 25 cc. of 4% absolute methanolic solution of hydrochloric acid. After the liquid was refluxed for thirty minutes, it was poured into crushed ice, the mixture was diluted with water and the ester was removed by filtration. The yield was 0.9 g. When recrystallized from dilute methanol it consisted of thin plates and rhombs which melted at 174°. In parallel polarized light (crossed nicols) only partial extinction of many of the plates occurred when the microscope stage was revolved. Partial biaxial interference figures were frequently shown in convergent polarized light (crossed nicols). Double refraction was extremely strong: η_α, 1.535 (common); η_β, indeterminate; η_γ, 1.740; both ± 0.003.

Anal. Calcd. for $C_{24}H_{28}O_9$: OCH_3 (3), 20.2. Found: OCH_3, 20.2.

Diacetyldihydrotoxicarolic Acid Methyl Ester.—One gram of the methyl ester dissolved in a mixture of 6 cc. of pyridine and 8 cc. of acetic anhydride was allowed to stand for three hours. The solution was then poured into 100 cc. of water, and the aqueous liquid was decanted from the yellow oil which adhered to the flask. The latter was washed several times with water and then dissolved in boiling methanol. Upon adding water to the solution until a slight turbidity was produced, 0.9 g. of the diacetate crystallized. It was recrystallized from its solution in hot methanol obtained by dissolving the material in chloroform, adding ten volumes of methanol and boiling the solution until the chloroform was removed. It separated as groups of rods, which melted at 143–144°.

Anal. Calcd. for $C_{28}H_{32}O_{11}$: acetyl, 15.81; OCH_3 (3), 17.10. Found: acetyl, 14.4; OCH_3, 17.06.

Derric Acid from Dihydrotoxicarolic Acid.—Dihydrotoxicarolic acid was oxidized with alkaline hydrogen peroxide according to the directions given for the preparation of derric acid from deguelic acid.[15] The product obtained melted at 168° and was shown by comparison with an authentic sample to be derric acid.

Dehydrotoxicarol Monocarboxylic Acid.—One gram of dehydrotoxicarol, suspended in 25 cc. of boiling ethanol, was quickly dissolved by the addition of 4 cc. of 50% aqueous potassium hydroxide solution. Four cc. of 30% hydrogen peroxide diluted with 6 cc. of water was then added at once, and the reaction was allowed to continue for *fifteen seconds.* One hundred twenty-five cc. of water was then quickly added, and the solution was filtered from a small quantity of unchanged starting material. The filtrate was then four-fifths neutralized with sulfuric acid, after which acetic acid was added until a slight turbidity resulted. The liquid was now allowed to crystallize. The yield of the acid was 0.75 to 0.9 g. The material, when recrystallized from dilute alcohol and thoroughly dried at 75° under reduced pressure, melted at 230° with the evolution of gas. It gave a dark green color with ferric chloride.

[15] Clark, THIS JOURNAL, **53**, 2370 (1931).

Anal. Calcd. for $C_{23}H_{22}O_9$: mol. wt., 442.3; C, 62.43; H, 5.01; OCH_3 (2), 14.03. Found: mol. wt. (titration), 448; C, 62.53; H, 5.12; OCH_3, 14.0.

Risic Acid from Dehydrotoxicarol Monocarboxylic Acid.—One-tenth gram of the monocarboxylic acid was dissolved in an aqueous potassium hydroxide solution and boiled with 2 cc. of 30% hydrogen peroxide until the liquid became practically colorless. Upon acidifying the solution with sulfuric acid, a crystalline precipitate formed, which melted at 262°. This material was proved, by comparison with an authentic sample, to be risic acid.

Dihydrodehydrotoxicarol Monocarboxylic Acid.—A solution of 2.5 g. of dehydrotoxicarol monocarboxylic acid in 250 cc. of hot ethanol was reduced with hydrogen and the platinum catalyst of Voorhees and Adams.[13] The resulting solution was filtered from the catalyst, evaporated to 50 cc., diluted with water until a slight turbidity resulted, and then allowed to crystallize. The yield was 2 g. The material was recrystallized from a hot acetic acid solution by the addition of two volumes of hot water. It separated as stout rods, which when dried under reduced pressure at 75° effloresced. The anhydrous material melted at 211° with the evolution of gas. It gave a purple color with ferric chloride.

Anal. Calcd. for $C_{23}H_{24}O_9$: C, 62.15; H, 5.44; OCH_3 (2), 13.97. Found: C, 62.20; H, 5.54; OCH_3, 14.0.

Monoacetyldehydrotoxicarol Monocarboxylic Acid.—A mixture of 1 g. of free acid, 10 cc. of 5% potassium hydroxide, 10 g. of ice and 1 cc. of acetic anhydride was shaken for two minutes. The liquid was then acidified to Congo red, causing 1.1 g. of crude product to separate. This material was dissolved in 15 cc. of hot methanol. The solution was filtered through norit and then treated with 10 cc. of hot water. Crystallization began at once and yielded 0.7 g. of crystalline acetyl compound. It was recrystallized from its solution in hot methanol by adding an equal volume of hot water. It consisted of colorless rods which melted at 163°. It gave a faint greenish-yellow color with ferric chloride.

Anal. Calcd. for $C_{25}H_{24}O_{10}$: C, 61.98; H, 5.00; OCH_3 (2), 12.8; acetyl, 8.88. Found: C, 61.97; H, 5.08; OCH_3, 13.1; acetyl, 8.7.

Summary

Experimental evidence herewith presented concerning the formation and reactions of apotoxicarol, dihydrotoxicarolic and dehydrotoxicarol monocarboxylic acids, when considered in conjunction with previously published data, demonstrates that quite probably the configuration of toxicarol is that represented by formula VIII (in the text). At this time no suggestion concerning the nature of the C_5H_7O grouping or its position or positions of attachment to ring *d* will be made.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

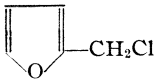
REARRANGEMENT OF THE ALPHA-FURFURYL GROUP. II. 5-METHYLFURFURYL CHLORIDE AND 5-METHYLFURYLACETIC ACID[1]

BY E. W. SCOTT AND JOHN R. JOHNSON

RECEIVED MARCH 23, 1932 PUBLISHED JUNE 6, 1932

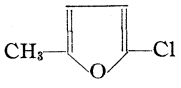
It has been observed[2] recently that the nitrile obtained by the action of α-furfuryl chloride upon aqueous sodium cyanide produces 5-methylfuroic acid upon hydrolysis, but the experimental data are too meager to fix with certainty the exact stage at which the rearrangement occurs. The present study was undertaken with the object of establishing this point and of investigating the mechanism of the rearrangement.

The possibility of a rearrangement of α-furfuryl chloride (I) into the isomeric 5-methyl-2-chlorofuran (II), or a dynamic isomerism of these halides, was considered to be unlikely on theoretical grounds. The synthesis of 5-methyl-2-chlorofuran through the decarboxylation of 2-methyl-5-chloro-3-furoic acid[3] now excludes definitely this possibility, since the two halides are found to be entirely distinct individuals. The relationship between them is analogous to that of benzyl chloride and the chlorotoluenes; α-furfuryl chloride has the higher boiling point and the more labile halogen atom. Likewise, the possibility of a rearrangement during hydrolysis of the nitrile has now been excluded through the synthesis of



B. p. 49.6–50° at 27 mm.

I



B. p. 48–49° at 70 mm.

II

authentic 5-methyl-2-furonitrile, by the dehydration of 5-methylfurfuraldoxime. A comparison of the physical properties of 5-methyl-2-furonitrile and of α-furfuryl cyanide with those of the nitrile obtained from α-furfuryl chloride and aqueous sodium cyanide, indicate that the latter is a mixture of approximately 85% 5-methyl-2-furonitrile and 15% α-furfuryl cyanide. This result demonstrates clearly that the rearrangement of the α-furfuryl group occurs in the production of the nitrile.

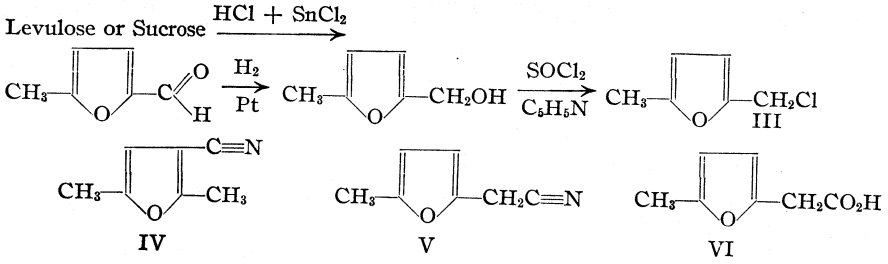
In dealing with the mechanism of rearrangement it seemed of interest to prepare a derivative of α-furfuryl chloride with a substituent in the 5-position and to observe its behavior toward aqueous sodium cyanide.

[1] This article is an abstract of a portion of a thesis submitted by E. W. Scott to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in July, 1931.

[2] (a) Reichstein, *Ber.*, **63**, 749 (1930); (b) Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930).

[3] This synthesis was carried out by Mr. G. F. Rundel.

5-Methylfurfuryl chloride (III) was selected for this purpose and was synthesized through the reactions indicated below.

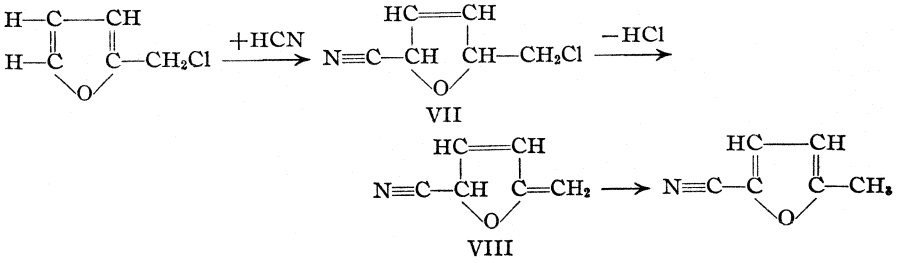


Since the 5-position in this halide is blocked, the reaction with sodium cyanide might give the normal product, 5-methylfuryl-2-acetonitrile (V), or a product of rearrangement, 2,5-dimethyl-3-furonitrile (IV), in which the cyano group entered the 3-position of the ring. Upon hydrolysis the latter would give rise to the known 2,5-dimethylfuroic acid (m. p. 134°), and the former would yield 5-methylfuryl-2-acetic acid. The nitrile actually obtained in this reaction, upon hydrolysis with aqueous potassium hydroxide and subsequent acidification, gave an acid melting at 57–58°, presumably 5-methylfuryl-2-acetic acid (VI). To establish the identity of this acid, an authentic specimen was synthesized from 5-methylfurfural, through the series of reactions which had been used to obtain 2-furylacetic acid from furfural.[2b,4] The authentic acid melted at 57–58° and showed no depression of the melting point when mixed with the acid obtained from 5-methylfurfuryl chloride.[5] This result indicates that the rearrangement requires the presence of a hydrogen in the 5-position, and that the 3- and 5-positions in the furan ring do not have the close relationship shown by the ortho and para positions in the benzene ring.

To account for the formation of 5-methylfuronitrile from α-furfuryl chloride, Reichstein[2a] has postulated an unstable intermediate compound (VIII) but has not proposed a mechanism to account for its production. The formation of this unstable structure (VIII) can be accounted for by rearrangement of the α-furfuryl group in the course of the reaction, but it seems more likely that the first step is a 1,4-addition of hydrogen cyanide

[4] In a private communication this result was reported to Dr. Reichstein, who informed us that he had carried out a similar investigation and had observed the same result. In a recent article Reichstein and Zschokke [*Helv. Chim. Acta*, **15**, 249 (1932)] have described a synthesis of 5-methylfuryl-2-acetic acid by an entirely independent method, from 5-methylfuroyl chloride. They reported that the synthetic acid melted at 61–62°, and was identical with the acid obtained from 5-methylfurfuryl chloride. This halide was prepared from 5-methylfurfuryl alcohol, obtained by reduction of 5-hydroxymethylfurfural.

[5] It is probable that none of the isomeric 2,5-dimethyl-3-furoic acid is produced from 5-methylfurfuryl chloride, since this acid is sparingly soluble in water and could be detected readily.



(VII). This addition would be followed by elimination of hydrogen chloride and rearrangement of the resulting 5-methylene-2,5-dihydro-2-furonitrile (VIII) into 5-methylfuronitrile.

The postulation of 1,4-addition to the furan ring finds support in the interpretation of the behavior of furan derivatives in halogenation, nitration and ring-opening reactions. 1,4-Addition of hydrogen cyanide to the furan ring may occur, likewise, in the synthesis of aldehydes[6] by the action of hydrogen cyanide on furan in the presence of hydrogen chloride. The observation that the aldehyde synthesis can be effected with furan derivatives containing one substituent in the 2- or 5-position, but is unsuccessful when substituents are present in both positions, can be explained satisfactorily by this hypothesis. An investigation of the addition of hydrogen cyanide to various types of furan derivatives and to conjugated aliphatic systems is now in progress.

In comparing the aromatic character of the benzene and furan rings it is of interest to note that the analogous benzene derivative, benzyl chloride, does not undergo rearrangement on treatment with sodium cyanide.[7] This difference can be interpreted as an indication of the ethylenic, or non-aromatic, character of the furan ring and places the simple furan derivatives in an intermediate position between the 1,3-butadienes and benzene. In the benzene series the aromatic[9] character of the ring is augmented by the presence of certain substituents (COOH, NO_2, SO_3H) and is decreased by the presence of others (OH, NH_2). In the furan series an analogous effect is observed: the presence of certain substituents (especially COOH) increases the aromatic character of the ring, and the pres-

[6] Reichstein, *Helv. Chim. Acta*, **13**, 345 (1930).

[7] No *o*- or *p*-tolunitrile could be detected in the nitrile produced by the reaction of benzyl chloride or benzyl iodide with sodium cyanide. On the other hand, benzylmagnesium chloride undergoes abnormal reaction with certain substances and gives rise to *o*-tolyl derivatives.[8]

[8] Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); Austin and Johnson, *ibid.*, **54**, 647 (1932).

[9] It is difficult to formulate a concise definition of the term aromatic. It is used here to mean a closely integrated, cyclic, conjugated system (containing two or more double bonds) characterized by a marked tendency to resist alteration of the conjugated system and rupture of the ring (especially through oxidation).

ence of others (OH, NH_2) causes a marked decrease of stability and a closer approach to the unsaturated aliphatic type. Since the thiophene ring is generally considered to be one of the most highly aromatic heterocycles, it would be of interest to investigate the behavior of the thiophene analog of α-furfuryl chloride, 2-chloromethylthiophene, toward aqueous sodium cyanide. A study of this reaction is in progress.

Experimental

5-Chloro-2-methyl-3-furoic Acid.—Ethyl 2-methyl-3-furoate was obtained by Benary's[10] modification of the Feist synthesis, from 1,2-dichloroethyl ether and acetoacetic ester. It was found advantageous to use aqueous pyridine[11] in effecting this reaction instead of ammonia, since the production of a pyrrole derivative is thereby obviated and the yield of the furan derivative is increased to 50–60% of the theoretical.

The chlorination of ethyl 2-methyl-3-furoate was carried out in the manner described by Hill and Jackson[12] for the chlorination of ethyl furoate. The ester was heated in a distilling flask in an oil-bath at 145°, and a stream of dry chlorine was introduced beneath the surface of the liquid. When the gain in weight attained 80–90% of the amount calculated for the introduction of one chlorine atom, the chlorination was stopped. The reaction mixture was saponified by heating with an excess of alcoholic sodium hydroxide solution, and after adding water the alcohol was distilled off. After pouring into dilute hydrochloric acid, the crude acid was filtered with suction and washed with a small quantity of water. After recrystallization from hot water, 5-chloro-2-methyl-3-furoic acid separated in glittering plates, m. p. 122–123° (uncorr.). The yield was 35–50% of the theoretical.

Anal. Calcd. for $C_6H_5O_3Cl$: Cl, 22.1. Found: Cl (Parr bomb), 21.85, 22.00. Neutralization equivalent: calcd., 160.5; found, 161.3.

In this product the chlorine is shown to be attached in the ring and not in the side chain since it is not removed by heating with alcoholic sodium hydroxide solution. It is inferred with reasonable certainty that the halogen entered the 5-position in preference to the 4-position, since the introduction of halogens always occurs by preference in an α-position of the furan ring. Experiments are in progress with a view to establishing the position of the halogen by means of a direct proof of structure.

5-Methyl-2-chlorofuran.—5-Chloro-2-methyl-3-furoic acid was decarboxylated in 5-g. portions by heating in the presence of high-boiling coal tar bases (b. p. 150–200° at 16 mm.) and copper bronze.[13] The decomposition began at 250–260°, and was quite rapid at 260–270°. From 33 g. of the acid there was obtained 12 g. of 5-methyl-2-chlorofuran (50% yield). The purified product was a colorless liquid with an odor resembling that of chloroform; b. p. 108–110° at 740 mm., 48–49° at 70–75 mm., n_C^{20} 1.4579, n_D^{20} 1.4611, n_F^{20} 1.4714, n_G^{20} 1.4781, d_{20}^{20} 1.1204, d_4^{20} 1.1184; MR_D (calcd.) 28.67, (obs.) 28.56.

Anal. Calcd. for C_5H_5OCl: Cl, 30.44. Found: Cl (Parr bomb), 29.90, 30.55.

This halide is distinctly different from α-furfuryl chloride, for which Kirner[14] re-

[10] Benary, *Ber.*, **44**, 493 (1911).

[11] This modification was developed by Mr. M. O. Baker. Details of the method will be published elsewhere.

[12] Hill and Jackson, *Proc. Am. Acad. Arts Sci.*, **24**, 320 (1888).

[13] Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930).

[14] Kirner, THIS JOURNAL, **50**, 1959 (1928).

ported the following constants: b. p. 49.6–50° at 27 mm., d_{20}^{20} 1.1804, d_4^{20} 1.1783, n_D^{20} 1.4941; MR_D (obs.) 28.788. 5-Methyl-2-chlorofuran is considerably more stable than α-furfuryl chloride toward metathetical reagents, has no lachrymatory action and does not undergo rapid spontaneous decomposition on standing. Samples of this halide have been kept for more than six months (under alkaline hydroquinone) without appreciable resinification.

5-Methylfurfural.—After preliminary experiments had been made, in which 5-chloromethylfurfural was isolated and reduced with stannous chloride, it was found that the desired aldehyde could be obtained directly by heating levulose, inulin or sucrose with dilute mineral acid in the presence of stannous chloride. Although the yield is low, this modification decreases the time required and is far less tedious than other methods.

In a 12-liter round-bottomed flask fitted with a separatory funnel and a short fractionating column, 500 g. of technical stannous chloride crystals, 2 kg. of sodium chloride and 4 liters of 12% sulfuric acid were mixed thoroughly and heated to boiling over a large gas-plate. When vigorous ebullition began, a solution of 800 g. of sucrose in 1 liter of hot water was added slowly through the separatory funnel over a period of thirty to forty-five minutes. The aldehyde distils out rapidly as it is formed, and an efficient condenser is necessary to avoid loss. The distillation was continued after all the sucrose had been added, until the distillate came over colorless. The entire distillate was carefully neutralized with sodium carbonate, saturated with sodium chloride and distilled. From the second distillate, which had separated into two layers, the methylfurfural was removed by several extractions with benzene. After distilling off practically all of the benzene, the residue was distilled under reduced pressure; b. p. 94–95° at 52 mm., 106–107° at 60 mm. The freshly distilled methylfurfural is an almost water-white liquid, but it darkens quickly on standing; it distils under atmospheric pressure at 179–184°, with slight decomposition. The yields in the above preparation varied from 8–14% of the theoretical (on the basis of the levulose residue only); usually 27–35 g. (10–13% yield) of 5-methylfurfural was obtained in a single preparation.

The 5-methylfurfural was identified by several reactions. On treatment with aqueous ammonia it gave methylhydrofuramide, m. p. 84–85° (reported 86–87°); with hydroxylamine it gave an oxime (described below). This aldehyde underwent the Cannizzaro reaction with the production of 5-methylfuroic acid, m. p. 107–108°, and 5-methylfurfuryl alcohol; in the Perkin reaction with acetic anhydride and sodium acetate it gave 5-methylfurylacrylic acid, m. p. 153–154°.

5-Methylfuronitrile from 5-Methylfurfural.—In order to obtain a pure specimen of 5-methylfuronitrile for comparison with the nitrile obtained from furfuryl chloride this substance was prepared by the dehydration of 5-methylfurfuraldoxime.

Twenty-two grams (0.2 mole) of freshly distilled 5-methylfurfural was mixed with a solution of 25 g. of hydroxylamine sulfate and 35 g. of sodium acetate crystals in 250 cc. of water, and the mixture was allowed to stand at 20°. After the first hour a heavy semi-solid mass had separated but after twenty-four hours the reaction mixture contained a mass of long pale yellow needles. These were filtered with suction and found to melt at 110–112°, corresponding to the form described by Fromherz and Meigen[15] as the *syn*-form of the oxime (m. p. 112°). Ether extraction of the aqueous filtrate gave an additional quantity of crystals which melted at 104–108°. The two fractions, amounting to 25 g., were combined for the next preparation.

Twenty-five grams of crude 5-methylfurfuraldoxime was dissolved in 42 g. of acetic anhydride and the solution was boiled gently for three minutes. After cooling

[15] Fromherz and Meigen, *Ber.*, **40**, 403 (1907).

the solution was poured carefully into a slight excess of sodium carbonate solution and was subjected to steam distillation. The 5-methylfuronitrile was extracted from the distillate with ether, and after drying over anhydrous magnesium sulfate was distilled under reduced pressure; b. p. 65–67° at 15 mm. The yield was 13 g. (67% yield, based upon 5-methylfurfural). 5-Methylfuronitrile is a colorless liquid with an agreeable aromatic odor; it is appreciably soluble in water and is miscible with the usual organic solvents. For analysis and determination of physical constants, the material was carefully refractionated under diminished pressure: b. p. 74–75° at 27 mm., n_D^{20} 1.4848, d_4^{20} 1.0399, d_4^{25} 1.0348; MR_D (calcd.) 28.24, MR_D (obs.) 29.49. A Kjeldahl analysis gave 12.77% N; calcd. for C_6H_5ON, N, 13.08.

For comparison, the physical properties of the nitrile obtained from α-furfuryl chloride (A), pure 5-methyl-2-furonitrile (B) and α-furfuryl cyanide (C) are given.

(A) Nitrile from C_4H_3O-CH_2Cl:[16] b. p. 74–75° (26 mm.); d_4^{20} 1.0463; n_D^{20} 1.4833; MR_D (obs.) 29.24

(B) 5-Methyl-2-furonitrile: b. p. 74–75° (27 mm.); d_4^{20} 1.0399; n_D^{20} 1.4848; MR_D (obs.) 29.49

(C) α-Furfuryl cyanide: b. p. 78–80° (20 mm.); d_4^{25} 1.0854; n_D^{25} 1.4715; MR_D (obs.) 27.60

A rough calculation from these data indicates that the nitrile from α-furfuryl chloride described by Kirner and Richter[16] contained approximately 85% of 5-methylfuronitrile and 15% of α-furfuryl cyanide.

5-Methylfurfuryl Alcohol.—5-Methylfurfural was converted into the corresponding alcohol by catalytic hydrogenation, following the method of Adams and Kaufmann[17] for the preparation of furfuryl alcohol from furfural. After careful fractionation, the alcohol distilled at 70–73° (6 mm.), or 97–99° (36 mm.). The yields were 65–70% of the theoretical. The preparation of this alcohol has been described previously by Blanksma,[18] who obtained it by treating 5-methylfurfural with strong potassium hydroxide solution. He reported a boiling-point of 100° at 11 mm., which is widely different from that observed in the present work, but gave no other physical constants.

5-Methylfurfuryl alcohol is a colorless liquid of pleasant odor; it is quite soluble in water and is miscible with alcohol and ether. Under atmospheric pressure (744 mm.) it boils with slight decomposition at 194–196°. A sample freshly distilled under reduced pressure had the following constants: d_4^{20} 1.0769, n_D^{20} 1.4853; MR_D (calcd.) 29.94, (obs.), 29.83. The diphenylurethan was prepared by heating for thirty minutes 1 g. of the alcohol and 1 g. of diphenylcarbamyl chloride in 5 cc. of pyridine. After two crystallizations from petroleum benzine (b. p. 60–70°), the diphenylurethan was obtained as a white crystalline solid, m. p. 52–53°.

5-Methylfurfuryl Chloride.—5-Methylfurfuryl alcohol was converted into the chloride by the method that Kirner used for the preparation of furfuryl chloride from furfuryl alcohol.[14] Since this chloride appeared to be even more unstable than furfuryl chloride, the product was not isolated but was prepared in ethereal solution and used directly for the next step.

5-Methylfurfuryl Cyanide (5-Methylfuryl-2-acetonitrile) and 5-Methylfuryl-2-acetic Acid.—An ethereal solution of 5-methylfurfuryl chloride, prepared from 18 g. (0.15 mole) of 5-methylfurfuryl alcohol, was treated with aqueous sodium cyanide according to the procedure of Kirner and Richter.[16] Steam distillation of the reaction

[16] Kirner and Richter, THIS JOURNAL, **51**, 3131 (1929).

[17] Adams and Kaufmann, *ibid.*, **45**, 3029 (1923).

[18] Blanksma, *Chem. Weekblad*, **9**, 186 (1912).

mixture gave 2.0 g. (11% yield) of 5-methylfurfuryl cyanide, which separated as a pale straw colored liquid sparingly soluble in water.

The nitrile was hydrolyzed by boiling with 20% potassium hydroxide solution, and after acidification the acid was removed by ether extraction. After two recrystallizations from petroleum benzine, there was obtained 0.5 g. (25% yield) of colorless crystals of 5-methylfuryl-2-acetic acid, m. p. 57–58°. This acid showed no depression of the melting point when mixed with an equal quantity of authentic 5-methylfuryl-2-acetic acid synthesized from 5-methylfurfural. None of the isomeric 2,5-dimethylfuroic acid (m. p. 134°) was detected in the reaction products.

5-Methylfuryl-2-acetic Acid from 5-Methylfurfural.—This synthesis was effected through the series of reactions used previously for the preparation of 2-furylacetic acid from furfural.[2b] Fifty-five grams (0.5 mole) of 5-methylfurfural was condensed with 30.5 g. of nitromethane (0.5 mole) in the presence of aqueous potassium hydroxide, according to the procedure of Thiele and Landers.[19] After one crystallization from benzene, the 5-methylfurylnitroethylene was obtained in yellow crystals, m. p. 75–76°. An ethereal solution of this substance was reduced with zinc and acetic acid to 5-methylfuryl-2-acetaldoxime. The crude oxime was boiled for three minutes with an excess of acetic anhydride and the resulting solution was poured into an excess of sodium carbonate solution. Steam distillation of the alkaline solution gave 3 g. of 5-methylfurfuryl cyanide, which was hydrolyzed by boiling for one hour with an excess of 30% aqueous potassium hydroxide. Upon acidification there was obtained 1.5 g. of 5-methylfuryl-2-acetic acid, which after two crystallizations from petroleum benzine (b. p. 60–70°) formed colorless needles, m. p. 57–58°. This acid is moderately soluble in cold water, and is very soluble in alcohol, acetone and ether. The observed neutralization equivalent was 142.0 (calcd. 140).

2,5-Dimethylfuroic Acid.—For purposes of comparison, this isomer of 5-methylfuryl-2-acetic acid was prepared from the monoethyl ester of methronic acid (5-methyl-4-carboxyfuryl-2-acetic acid), which was obtained by warming ethyl acetoacetate with sodium succinate and acetic anhydride.[20] Since it is not known definitely whether the esterified carboxyl group in this ester is the one attached in the ring or that in the side chain, the reactions were carried out in such a way that the position of the esterified carboxyl group could be determined. This was accomplished by subjecting the monoethyl ester to decarboxylation, hydrolyzing the resulting ester and identifying the corresponding acid. Since the latter proved to be 2,5-dimethylfuroic acid, the esterified carboxyl in monoethyl methronate is shown definitely to be the one attached in the ring. If the side chain carboxyl had been esterified, 5-methylfuryl-2-acetic acid would have been the final product.

The decarboxylation of monoethyl methronate was followed in an approximately quantitative manner, as described previously for the decarboxylation of 2-furylacetic acid.[2b] A sample of 5.222 g. (0.026 mole) of monoethyl methronate (m. p. 73–74.5°) on heating for thirty minutes in an oil-bath at 290–300° gave 0.860 g. (0.020 mole) of carbon dioxide and 3.462 g. (0.021 mole) of ethyl 2,5-dimethylfuroate. These quantities correspond, respectively, to 77 and 80% of the theoretical. The liquid distillates from several decarboxylations were united, washed with dilute alkali to remove undecomposed acid, dried and distilled under diminished pressure. Upon redistillation ethyl 2,5-dimethylfuroate (ethyl pyrotritarate)[21] was obtained as a colorless liquid with a very characteristic aromatic odor: b. p. 83–85° at 6 mm., 99–101° at 14 mm.,

[19] Thiele and Landers, *Ann.*, **369**, 303 (1909).

[20] Fittig and v. Eynern, *ibid.*, **250**, 178 (1889).

[21] We are indebted to Dr. R. C. Tallman for the determinations of several of the physical constants here reported.

d_4^0 1.0718, d_4^{20} 1.0537, d_4^{23} 1.0490, n_C^{20} 1.46535, n_D^{20} 1.46897, n_F^{20} 1.47812, n_G^{20} 1.48607; MR_D (calcd.) 43.93, (obs.) 44.43. This ester has previously been described by Brühl,[22] who reported: $n_D^{23.1}$ 1.46862, $d_4^{23.1}$ 1.0478.

Two grams of the ester was hydrolyzed by refluxing for several hours with 2 g. of potassium hydroxide dissolved in 50% alcohol. After distilling off the alcohol, the cooled alkaline solution was poured into ice-cold 5% hydrochloric acid. The precipitated 2,5-dimethylfuroic acid was filtered with suction and dried; without further purification the acid melted at 132.5–133.5 (corr.). After crystallization from petroleum benzine (b. p. 100–110°), the acid formed white needles, m. p. 134°. This acid has previously been obtained by several methods; the melting points reported by various investigators lie in the range 133–135°.[23]

Summary

It has been shown that rearrangement of the α-furfuryl group into the 5-methylfuryl group occurs in the reaction of α-furfuryl chloride with aqueous sodium cyanide. The resulting nitrile contains approximately 85% of 5-methyl-2-furonitrile and 15% of α-furfuryl cyanide.

5-Methylfurfuryl chloride was synthesized and was found to react normally with aqueous sodium cyanide to give 5-methylfuryl-2-acetonitrile. The latter upon hydrolysis gave 5-methylfuryl-2-acetic acid. This acid was also synthesized by an independent method from 5-methylfurfural.

It is suggested that the mechanism of the rearrangement reaction involves 1,4-addition of hydrogen cyanide to the furan ring.

[22] Brühl, *J. prakt. Chem.*, [2] **50,** 143 (1894).

[23] Wislicenus and Stadnicky, *Ann.*, **146,** 306 (1868); Böttinger, *ibid.*, **172,** 241 (1874); Harrow, *ibid.*, **201,** 145 (1880); Fittig and v. Eynern, *ibid.*, **250,** 190 (1889); Fittig and Parker, *ibid.*, **267,** 212 (1892).

ITHACA, NEW YORK

NOTES

The Preparation of Tetrathiopentone

BY STEPHEN A. KARASIEWICZ

In the course of attempts to iodize oleic acid by means of hydrogen sulfide and iodine, employing acetone as solvent, it was observed that white crystals of tetrathiopentone, $C_{15}H_{28}S_4$, were formed as a by-product of the reaction. This substance was first described by Fromm and Baumann.[1]

The course of the reaction between iodine, hydrogen sulfide and acetone is probably analogous to the method of Fromm and Baumann, who used concentrated hydrochloric acid, hydrogen sulfide and acetone, since there is

[1] Fromm and Baumann, *Ber.*, **22,** 1044 (1889).

conversion of iodine into hydriodic acid during the reaction. A larger yield is obtained from the new method, as 20 g. of tetrathiopentone is obtained from 60 cc. as compared to 16 g. from 100 cc. of acetone. In repeating the Fromm and Baumann method only 3 g. of tetrathiopentone was obtained. The method of preparation and purification used for tetrathiopentone during this study also appeared easier. The substance crystallizes readily from the acetone and when filtered and washed with fresh acetone is pure.

When tetrathiopentone was reduced in liquid ammonia with sodium, isopropyl mercaptan was isolated and identified as the 3,5-dinitrobenzoyl derivative.[2]

Experimental.—Twenty grams of pulverized iodine is dissolved in 60 cc. of acetone and a stream of hydrogen sulfide is passed through this solution for seven hours. Fresh acetone should be added to replace that evaporated by the heat evolved at the beginning of the reaction. The completion of the reaction is marked by a reddish-brown discoloration of the solution and by the appearance of white crystals, which increase in number upon standing in the refrigerator. The crystals are filtered and carefully washed with acetone, in which they are sparingly soluble. When 30 cc. of oleic acid is added to the above solution and hydrogen sulfide used as previously, there appear at the interface between the two non-miscible layers very pure crystals of tetrathiopentone.

These crystals, recrystallized from acetone or alcohol, melted sharply at 170–171°. The mixture melting point of equal amounts of tetrathiopentone made by both methods was 170–171°.

Mol. wt. (Camphor method).[3] Calcd. for $C_{15}H_{28}S_4$: 336. Found: 333.4, 337.0.
Anal. Calcd. for $C_{15}H_{28}S_4$: S, 38.09. Found: S, 37.92, 38.13.

To 150 cc. of dry liquid ammonia in a Dewar flask is added 1 g. of powdered tetrathiopentone, which is treated with 0.3 g. of metallic sodium. After disappearance of the blue color ether is added and the ammonia allowed to evaporate. The remaining white precipitate is quickly filtered and covered with fresh ether. The suspension obtained is cooled in a salt–ice freezing mixture, while hydrogen chloride gas is passed through. When the ether solution was neutralized and the ether distilled, isopropyl mercaptan was isolated according to Wertheim's procedure. The lead salt of isopropyl mercaptan was also prepared.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY MEDICAL SCHOOL
CHICAGO, ILLINOIS

RECEIVED JANUARY 25, 1932
PUBLISHED JUNE 6, 1932

[2] Wertheim, THIS JOURNAL, **51**, 3662 (1929).

[3] Rast in Houben's "Die Methoden der organischen Chemie," Leipzig, 1925, Vol. I, p. 933.

Furan Reactions. III. Absorption of Furan Vapors

By Charles D. Hurd and A. R. Goldsby

Mixtures of furan and air were made by introducing furan from a pipet into a 2-liter flask. Using a stopcock attachment, this gas was readily transferred into the buret of a modified Orsat type apparatus.[1] Fuming sulfuric acid (8% SO_3) was found to absorb the furan quickly and quantitatively, hence it was used to determine the percentage by volume of furan in the gas. The mixtures which were studied below contained about 10% of furan. The fuming acid is immediately darkened in color as the furan reaches it.

Using 40% potassium hydroxide solution in an absorption pipet, only one-third of the furan content of the gas was removed after thirty passes in and out of the reagent. With alkaline potassium iodomercurate (the reagent for acetylene) or 52% sulfuric acid solution, about 35 to 40% of the furan was removed by seven two-minute passes. With 62.5, 67.5 and 72.5% sulfuric acid, the percentage of furan removed after seven passes, respectively, was 57, 90 and 95. Using 82.5% sulfuric acid, the furan was absorbed completely in three passes. The 82.5% acid is the reagent which is used for the absorption of propylene, α- and β-butylenes, butadiene, etc. Furan was also removed quantitatively with mercuric acetate solution (50 g. in 225 cc. of water) thereby forming[2] tetraacetoxymercurifuran, $C_4O(HgOAc)_4$. Unfortunately for its use in separating furan from other gases, this reagent also removes carbon dioxide and unsaturated hydrocarbons.

Conclusions.—Furan (gas) may be absorbed quantitatively by 82.5% sulfuric acid. A mixture of furan and ethylene could be analyzed in this manner since ethylene is not absorbed unless fuming sulfuric acid is used. The absorption method is not applicable for the quantitative analysis of furan when it is admixed with other unsaturated hydrocarbon gases. With such mixtures, liquefaction and distillation (by precise methods of fractionation) would be necessary for exact analysis.

Contribution from the
Department of Chemistry
Northwestern University
Evanston, Illinois

Received March 23, 1932
Published June 6, 1932

[1] Hurd and Spence, This Journal, **51**, 3357 (1929).

[2] Ciusa and Grilla, *Gazz. chim. ital.*, **57**, 323 (1927).

COMMUNICATIONS TO THE EDITOR

SIR JAMES IRVINE'S VIEW ON THE CONSTITUTION OF DI- AND POLYSACCHARIDES

Sir:

In a recent communication Irvine and McGlynn [THIS JOURNAL, **54,** 358 (1932)] comment on the use of 2,3,6-trimethylglucose as a reference substance in structural investigations and urge that "much further work and the application of new methods are alike necessary before definite constitutions can be assigned to the disaccharides and polysaccharides which are convertible into 2,3,6-trimethylglucose." These conclusions are valid in so far as work initiated by Irvine is concerned, but they do not represent the present state of carbohydrate chemistry. No less than six years ago, and before the publication of Irvine and Black's paper on maltose [*J. Chem. Soc.*, 862 (1926)] an explicit statement of the ambiguity caused by the use of 2,3,6-trimethylglucose as a reference substance was given by Charlton, Haworth and Peat [*ibid.*, 98 (1926)] and in the same year (1926) Haworth and Peat [*ibid.*, 3094 (1926)] developed a new experimental method which solved completely the problem left undecided by the isolation of a trimethylhexose as a scission product of a fully methylated disaccharide. This method has been employed to determine the constitution of maltose, lactose, cellobiose, melibiose, 4-glucosido-mannose and 4-glactosido-mannose [*ibid.*, 544, 1527, 2809, 3146 (1927); 1349, 1354 (1931)]. Recently its use has been extended to problems connected with the polysaccharides, starch, glycogen and xylan [Haworth and Percival, *ibid.*, 1342, 2850 (1931)]. In addition to the full treatment given in the original papers, an ample discussion of the various problems has appeared in a monograph [Haworth, "Constitution of Sugars," Edward Arnold and Co., London, 1929] and on various occasions in summary form [see, for example, *Helv. Chim. Acta*, 534 (1928)]. No reference whatever to any of this work is made by Irvine and McGlynn.

In describing the conversion of 2,3,6-trimethylglucose, *via* its γ-methylglucoside into tetramethyl-γ-glucose, the latter authors have not observed that this series of transformations was carried out by Schlubach and Bomhard in 1926 [*Ber.*, **59,** 845 (1926)]. Comment is necessary also on the conclusions drawn by Irvine and McGlynn from their experiments on the oxidation of 2,3,6-trimethylglucose. It is well known that in aqueous solution both γ- and δ-lactones enter into equilibrium with their parent acids. In those cases where both γ- and δ-lactones are obtainable from one acid (as with 2,3,6-trimethylgluconic acid) it is clear that no evidence of preferential oxidation to one particular lactone can be obtained by treatment of the sugar with bromine water, extraction of the aqueous solution with chloroform several hours after the commencement of the

reaction, and the mere isolation of that lactone on evaporation of the chloroform. Similar considerations apply when the oxidation is conducted in the presence of an excess of calcium carbonate, with the additional complication that under these conditions most of the product may pass through the stage of the calcium salt from which the organic acid, not the lactone, is liberated on acidification. The experimental procedure of these authors is ill-adapted to the problem they have in view and definite conclusions concerning the preferential formation of either lactone during the oxidation cannot be drawn from their present results.

CHEMISTRY DEPARTMENT
THE UNIVERSITY OF BIRMINGHAM
ENGLAND
E. L. HIRST

RECEIVED APRIL 13, 1932
PUBLISHED JUNE 6, 1932

THE EFFECT OF FOREIGN GASES ON UNIMOLECULAR REACTIONS

Sir:

The recent communication by Steacie [THIS JOURNAL, **54,** 1695 (1932)] suggests a generalization that has apparently not been made hitherto, *viz.*, that foreign gases do not activate unimolecular reactions. The earliest experimental evidence on this subject is the work of Daniels [THIS JOURNAL, **47,** 1602 (1925)], who showed that the rate of decomposition of nitrogen pentoxide in the presence of nitrogen falls off at about 0.01 mm. partial pressure. Later experiments show that the behavior is the same in the absence of nitrogen.

The conspicuous exception to this generalization is the action of hydrogen on certain organic compounds at elevated temperatures. The explanation of this exceptional behavior is to be sought in the fact that a reaction between the hydrogen and organic molecule would be predicted by an organic chemist.

While we do not know much about the conditions under which translational energy is converted into vibrational energy [see Kassel, Rice, *Chem. Rev.*, **10,** 11 (1932)], the evidence is that this process does not take place readily. The early attempts to calculate the limiting pressure for the unimolecular decomposition of nitrogen pentoxide were without significance because only translational energy was considered.

On the other hand, vibrational energy is only transferred readily when there is a sharp resonance between the colliding molecules.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
W. H. RODEBUSH
M. J. COPLEY

RECEIVED APRIL 25, 1932
PUBLISHED JUNE 6, 1932

POLYHALIDES CONTAINING FLUORINE

Sir:

The literature contains no evidence of the existence of polyhalides containing fluorine, save a mention by Cremer and Duncan [*J. Chem. Soc.*, **133**, 2243 (1931)], in a study of the dissociation pressures and other properties of the polyhalides, of the absorption of iodine bromide by cesium fluoride. On the basis of absorption taking place, they concluded that a compound, probably having the formula CsFIBr, was formed.

Several years ago work was started in this Laboratory on the preparation of polyhalides containing fluorine. We have found the following four methods for the preparation of alkali polyhalides containing fluorine.

(1) To a saturated solution of the alkali fluoride one equivalent of iodine is added and the solution chlorinated to the disappearance of the iodine color. On cooling crystals which were very nearly homogeneous were obtained.

(2) The same process as (1) with the modification of using a solution acidified with hydrochloric acid gave a better yield. Recrystallization of the products from either of these methods gave homogeneous anisotropic needle-like orange crystals.

(3) A mixture in the proportion of one molecule of alkali fluoride to one atomic weight of iodine was intimately mixed by grinding and chlorinated to constant weight. The final product was an orange-yellow solid which on recrystallization from water gave a good yield of the same orange-yellow crystals as before.

(4) To the acidulated saturated solution of the alkali fluoride was added a slight excess of an aqueous solution of iodine trichloride. The same orange-colored polyhalide immediately separated as gleaming needles.

Adsorbed water was carefully removed before analysis. Since the crystals tend to lose halogen, it is best to keep them in tightly stoppered bottles. The potassium salt is very unstable and so far we have been unable to get consistent analyses of it. However, the rubidium and cesium salts are quite stable, decomposing in the open air to white salts of the corresponding fluorides, respectively, at approximately 300°, and well above 300°.

Anal. Calcd. for $CsFICl_3$: Cs, 34.49; Cl, 27.62; I, 32.96. Found: Cs (perchlorate method), 34.27, 34.33; Cl, 27.61, 28.06; I, 33.38, 32.81.

The melting point of the $CsFICl_3$ in a sealed tube is 194°. The crystals exhibit parallel extinction and have a specific gravity of 3.565.

Anal. Calcd. for $RbFICl_3$: Rb, 25.30; Cl, 31.50; I, 37.58. Found: Rb, 25.27, 25.47; Cl, 31.46, 31.52; I, 37.52, 38.05.

The melting point of the $RbFICl_3$ in a sealed tube is 172°. It has a specific gravity of 3.159 and exhibits parallel extinction under crossed nicols.

The potassium salt has the same crystal form as the others and qualitative analysis shows the presence of potassium, chlorine, fluorine and iodine. The investigation of this and other polyhalides containing fluorine is being continued and will be reported in detail later.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO

HAROLD SIMMONS BOOTH
CARL F. SWINEHART
WILLIAM C. MORRIS

RECEIVED APRIL 30, 1932
PUBLISHED JUNE 6, 1932

THE ATOMIC WEIGHTS OF H(2) AND Be(9)

Sir:

Among the lighter elements there are two whose atomic weights are of especial interest at this period, H(2) and Be(9). Since H(2) is a probable nuclear building unit and is also the simplest complex nucleus reported to date (excluding neutrons) an accurate knowledge of its atomic weight gives a measure of the interaction energy of two protons and one electron, which energy may be a fundamental unit of the nucleus.

Another such unit may be the proton–electron interaction energy obtainable from the difference in mass of the neutron(1) and an atom of H(1). The accurate mass of Be(9) is necessary in calculating the mass of the neutron(1) [Chadwick, *Nature*, Feb. 27, 1932].

Until these atomic weights have been accurately determined we may predict values, that for H(2) being obtained by a simple calculation, based on the assumption that the lighter $4N + 2$ elements contain N α particles and one H(2) nucleus. Aston [*Proc. Roy. Soc.* (London), **A115,** 487 (1927)] gives for the packing fractions of Li(6) and B(10), 2.00 ± 0.10 and $1.35 \pm 0.05 \times 10^{-3}$ mass units (probable errors are assumed to be $^1/_3$ maximum allowable error). Using the packing fraction for helium, 0.54 ± 0.03, we obtain from the data for Li(6)

$$4(0.54 \pm 0.03) + 2A_1 = 6(2.00 \pm 0.10) + D_1$$
$$\text{or} \quad A_1 = (4.92 \pm 0.36) + D_1/2 \qquad (1)$$

and for B(10)

$$A_2 = (4.59 \pm 0.37) + D_2/2 \qquad (2)$$

where A_1 and A_2 represent the packing fraction of H(2) and the D's the mass defects of Li(6) and B(10) with respect to He(4) and H(2). Although these equations do not uniquely determine the packing fraction of H(2), they set a lower limit to its atomic weight at $(2.0098 + D_1 \pm 0.0007)$ from (1) and $(2.0092 + D_2 \pm 0.0007)$ from (2). From a consideration of the binding energies in some of the lighter nuclei, we may estimate values for the mass defects of Li(6) and B(10) to be $D_1 = 1.2 \pm 0.4$ and $D_2 = 2.4 \pm 0.6 \times 10^{-3}$ m. u. These values give H(2) an atomic weight of 2.0110

$\pm$ 0.0011 from (1) and 2.0116 $\pm$ 0.0013 from (2); mean *2.0113 $\pm$ 0.0012* (mass spectrograph scale). The agreement is satisfactory. This gives $4.3 \pm 1.2 \times 10^{-3}$ m. u. for the binding energy of the H(2) nucleus.

The chemical atomic weight of beryllium determined by Hönigschmid [*Ber.*, **55B**, 4 (1922)] is 9.018 $\pm$ 0.002. This is almost certainly too high, for while beryllium exists to 99.95% as Be(9) and to about 0.05% as Be(8) [Watson and Parker, *Phys. Rev.*, **37**, 167 (1931)], no isotope of mass number greater than 9 has been reported. Assuming the nucleus of Be(9) to contain 2 α particles, 1 proton and 1 electron, an upper limit for its atomic weight is 9.011 (chemical scale). This value has neglected the binding occurring between the constituents of the nucleus, which from disintegration experiments [Chadwick, *Proc. Roy. Soc.* (London), **A130**, 463 (1931)] has a value $5 \pm 2 \times 10^{-3}$ m. u., which is about that expected from the differences in mass defects of corresponding members of the $4N + 1$ and $4N$ series. Assuming this as a mass defect for Be(9), its atomic weight becomes 9.006 $\pm$ 0.002, and correcting for 1 part in 2000 of Be(8) gives *9.005 $\pm$ 0.002* for the atomic weight of beryllium. Since this is 0.013 m. u. less than the present chemical value a redetermination is necessary.

From the probable value of the mass of Be(9) and Chadwick's disintegration experiments we can make a rough estimate of the mass of the neutron(1), which indicates that it is little different from that of its isobar, H(1). If neutrons are formed exothermically from protons and electrons, it would seem highly probable that their formation could be effected in the laboratory and the energy change detected as radiation. The existence of H(2) nuclei [Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 164 (1932)] and neutrons(1) suggests that all known atomic nuclei could originate from protons and electrons through a succession of *two body collisions, e. g.*, 2H(2) nuclei $\longrightarrow$ 1 α particle, etc.

CHEMISTRY DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

NORMAN S. GRACE

RECEIVED MAY 5, 1932
PUBLISHED JUNE 6, 1932

KINETICS OF THE THERMAL DISSOCIATION OF GASEOUS ETHYL BROMIDE

Sir:

More exact experimental data on simple reactions are urgently needed for testing theories of unimolecular reactions, particularly with reference to the falling-off of the rate-constant at low pressures. The reaction

$$C_2H_5Br = C_2H_4 + HBr$$

has been studied for several years in this Laboratory, and a preliminary

report by E. T. Lessig is now in press. With improved technique and proper allowance for the reverse reaction, this reaction now appears to be as satisfactory a unimolecular reaction as any yet reported.

The data at pressures above 100 mm. in the range 390 to 420° are well expressed by the formula

$$k = 3.85 \times 10^{14} e^{-54,800/RT}$$

Below 120 mm. k falls off, and at 20 mm. it has only about one-third of its high pressure value. In this low pressure region the reaction appears to be purely second order. Calculations indicate 22 squared terms on the basis of present theories. Theory I of Rice and Ramsperger [THIS JOURNAL, **49,** 1617 (1927)] is not adequate to explain the facts. Temperature coefficients at the low pressures suggest that Kassel's Theory III [*J. Phys. Chem.*, **32,** 225 (1928)] may fit better than Theories II or I.

The addition of nitrogen, and of hydrogen, causes the value of k at low pressures to *decrease*. According to present accepted theories the addition of foreign gases should increase the value of k. Unless some unexpected specific chemical effect exists, the results suggest that certain aspects of present theories of unimolecular reactions should be critically reassessed.

The influence of other foreign gases of increasing complexity is now being investigated.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

E. L. VERNON
FARRINGTON DANIELS

RECEIVED MAY 9, 1932
PUBLISHED JUNE 6, 1932

THE EINSTEIN RELATION AND TEMPERATURE COEFFICIENT IN THE PHOTOBROMINATION OF CINNAMIC ACID

Sir:

Exact measurements on the photobromination of cinnamic acid, now in progress, show clearly that it is possible to obtain a quantum efficiency of 1 and a temperature effect of zero in agreement with simple photochemical theory, when accompanying thermal reactions are suppressed. They show, too, how the temperature coefficient of the total reaction can vary with the concentration.

The experiments were carried out in a quartz cell of 15-cc. capacity. Light of 4358 Å. was isolated from the spectrum of a capillary quartz mercury arc by means of a monochromator. The change in bromine concentration after fifteen minutes' illumination was measured and compared with the change in the control kept in the dark. The concentration of cinnamic acid was the same in all cases.

The results are summarized in the accompanying figure where Φ, the number of molecules of bromine consumed per quantum of light absorbed, is plotted against the concentration of bromine. This concentration is expressed in moles of bromine per liter of 0.00567 molar cinnamic acid in carbon tetrachloride. The reaction is a chain reaction, the products of the bromination apparently contributing some of their energy to activate new molecules of bromine.

The striking regularity with which Φ decreases as the dilution increases suggests that the energized products of the reaction gradually lose their activation by collision with the molecules of carbon tetrachloride. At infinite dilution the deactivation of products by the solvent should be so complete that no chain reaction is possible. Under these conditions, where secondary thermal reactions are eliminated, the quantum yield should be exactly 1. Extrapolation of the experimental curves to infinite dilution shows that this prediction is correct.

Furthermore, at infinite dilution where the reaction is purely photochemical, the temperature effect should be zero. Again the graphs support this prediction in a striking manner. The curves at 30 and 0° both extrapolate, within the limit of experimental error, to the same value of Φ, namely 1.

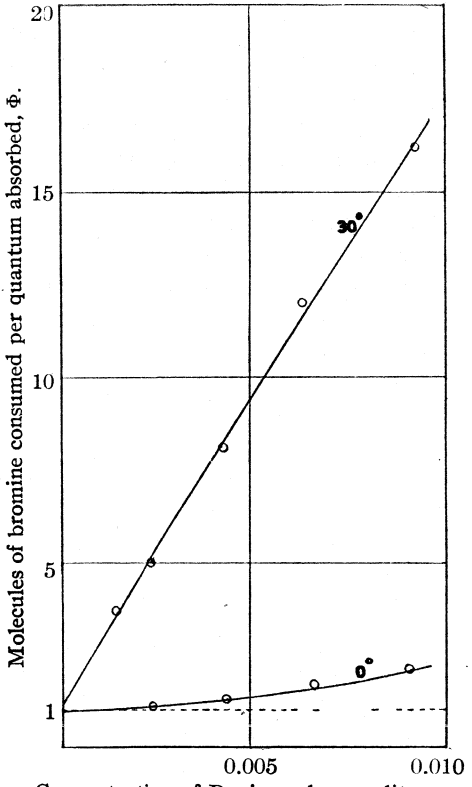


Fig. 1.—Photobromination of cinnamic acid in carbon tetrachloride.

In the more concentrated solutions the reaction is about eight times as fast at 30 as at 0°. The ratio of rates for a 10° difference in temperature is 1 at infinite dilution and increases to a limiting value of 2 in the more concentrated solutions. This value is in agreement with that of ordinary thermal reactions.

Experimental measurements and calculations are being continued.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

WALTER H. BAUER
FARRINGTON DANIELS

RECEIVED MAY 9, 1932
PUBLISHED JUNE 6, 1932

ISOLATION OF GLUTATHIONE FROM POTATO TUBERS TREATED WITH ETHYLENE CHLOROHYDRIN[1]

Sir:

Treatment of freshly-harvested potato tubers with ethylene chlorohydrin, a chemical that breaks their dormancy,[2] increases the sulfhydryl content of the expressed juice as shown by the nitroprusside test and by the sulfur reduction method.[3] In order to find whether this increase in sulfhydryl was due to an increase in glutathione, the procedure of Hopkins[4] for the isolation of glutathione was applied to the juice of potatoes treated with ethylene chlorohydrin.

Cut pieces of freshly-harvested potato tubers were dipped in a 1.6% solution of ethylene chlorohydrin, the excess solution drained off and the pieces placed in a closed container for twenty-four hours. They were then planted in moist soil for five days. After washing free of soil, the pieces were peeled, ground through a food chopper, the juice was expressed through cheesecloth, and the starch centrifuged out. The juice was boiled to coagulate the proteins, cooled, and filtered through glass wool. Following the procedure of Hopkins the cuprous salt of glutathione was isolated. In one experiment 1.5 liters of the boiled, filtered juice yielded 870 mg. The copper content was 17.48%; calcd., 17.26%.

The cuprous salt prepared by the above method was suspended in water and decomposed with hydrogen sulfide. After filtering out the cupric sulfide, the hydrogen sulfide was removed in a stream of hydrogen and the filtrate evaporated in a vacuum desiccator over sulfuric acid. When reduced to small volume, absolute alcohol was added and the glutathione allowed to crystallize. The yield from 395 mg. of the cuprous salt was 190 mg. of crystalline glutathione. An additional 70 mg. was obtained by bringing the mother liquor to dryness. The crystalline fraction was analyzed for nitrogen (micro Kjeldahl) and sulfur (Parr bomb).

Anal. Subs., 23.04 mg.: 10.8 cc. of $N/50$ H_2SO_4. Subs., 0.1141 g.: 0.0862 g. $BaSO_4$. Calcd. for $C_{10}H_{17}N_3SO_6$: N, 13.7; S, 10.42. Found: N, 13.1; S, 10.38.

By the same procedure, 970 mg. of the cuprous salt yielded 650 mg. of glutathione. This was recrystallized and the first fraction, which weighed 275 mg., was analyzed.

Anal. Subs., 30.99 mg.: 14.7 cc. of $N/50$ H_2SO_4. Subs., 0.1024 g.: 0.0771 g. $BaSO_4$. Found: N, 13.3; S, 10.34.

Using the same procedure, no glutathione could be isolated from the juice of untreated tubers, although qualitative tests indicated that a small

[1] Herman Frasch Foundation for Research in Agricultural Chemistry, Paper No. 36.

[2] Denny, *Am. J. Botany*, **13**, 118 (1926).

[3] Guthrie and Wilcoxon, *Contrib. Boyce Thompson Inst.*, **4**, 99 (1932).

[4] Hopkins, *J. Biol. Chem.*, **84**, 269 (1929).

amount was present. When potatoes that had been stored for several months were treated with ethylene chlorohydrin, the cuprous salt could be isolated, but in smaller yield than with freshly-harvested tubers. In one experiment, 1 liter of juice yielded 280 mg. of the cuprous salt; in another 600 cc. yielded 60 mg. The copper content of the latter preparation was 17.15%.

This is believed to be the first isolation of glutathione from a seed plant.

BOYCE THOMPSON INSTITUTE
FOR PLANT RESEARCH, INC.
YONKERS, NEW YORK

JOHN D. GUTHRIE

RECEIVED MAY 12, 1932
PUBLISHED JUNE 6, 1932

E. L. HIRST'S COMMENTS ON IRVINE AND McGLYNN'S PAPER ON "A POSSIBLE SOURCE OF ERROR IN DETERMINING THE CONSTITUTION OF DI- AND POLYSACCHARIDES"[1]

Sir:

The criticisms made by Dr. E. L. Hirst reveal that in his reading of the paper to which he refers he has overlooked the essential features of the work described. Constitutions are not assigned to di- and polysaccharides but attention is directed, systematically and on the evidence of experimental work described for the first time, to possible sources of error in determining the constitution of these compounds by the methylation method. It is the case that the possibility of 2,3,6-trimethylglucose functioning in both a normal and a γ-form has already been suggested but our omission of any reference to Schlubach and Bomhard [*Ber.*, **59**, 845 (1926)] does not involve that we overlooked previous work on the subject. It is at least unlikely that, as the originator of the method of solving the constitution of di- and polysaccharides by methylation, the efforts of other workers in this field should have been overlooked by me. But it may be pointed out that Schlubach and Bomhard merely converted the sugar into tetramethyl-γ-glucose through the intermediate formation of an unpurified glucoside, while in our case this glucoside was isolated after vacuum distillation as a pure compound, was analyzed and, among other reactions, was subjected to the graded hydrolysis which is obviously an essential part of the experimental scheme. The tautomerism of 2,3,6-trimethylglucose is in consequence no longer conjectural but is based on experimental evidence.

With regard to his criticisms of our studies on the oxidation of trimethylglucose, Dr. Hirst assumes that, when this reaction is carried out in the presence of calcium carbonate under the conditions we describe, the whole of the acid produced is transformed into the calcium salt. Such is

[1] Irvine and McGlynn, THIS JOURNAL, **54**, 358 (1932).

not the case and his criticism is pointless. The remaining papers he quotes were known to us.

THE UNIVERSITY, ST. ANDREWS, SCOTLAND JAMES C. IRVINE

RECEIVED MAY 20, 1932
PUBLISHED JUNE 6, 1932

AMMONIUM ACETATE AS A NEUTRAL BUFFERED STANDARD

Sir:

On theoretical grounds, Williams and Lyman [THIS JOURNAL, **54,** 1911 (1932)] point out that ammonium acetate should be a good buffer at the neutral point, with P_H value practically independent of concentration. They suggest it, therefore, as a practically useful standard for hydrogen ion work and accurate titrations to P_H 7, which can be prepared in one minute. They do not describe the method for preparing the solution, but the emphasis upon the brief time required and statement that concentration is of minor importance suggest that it is only necessary to dissolve a few grams of the dry salt in a little water to secure a standard solution accurately buffered at P_H 7.

In this Laboratory, ammonium acetate solutions buffered near P_H 7 have been much used in the extraction of exchangeable bases from soil. In a description of the procedures employed [Schollenberger and Dreibelbis, *Soil Science,* **30,** 161 (1930)] attention has been directed to the fact that solutions of "C. P. Analyzed Reagent" ammonium acetate in pure water are likely to be far from neutral; with several lots of the salt, normal solutions so prepared were near P_H 5, indicating the presence of about one mole of free acetic acid to two of ammonium acetate. Preparation of the solution by mixing equal volumes of accurately prepared 2 *N* solutions of acetic acid and ammonia was recommended. Experience has been that a solution so prepared is invariably very nearly neutral.

According to a well-known authority [Morley and Muir, "Watt's Dictionary of Chemistry," 1899, Vol. I, p. 9], pure ammonium acetate may be prepared by saturating glacial acetic acid with dry ammonia, and is then dry, white and odorless. It is difficult to crystallize, the aqueous solution tending to lose ammonia on evaporation, leaving an acid salt.

The crystalline salt sold as a reagent is often quite moist, with a strong odor of acetic acid, indicating either improper preparation or subsequent deterioration. Hence, a solution of commercial reagent quality ammonium acetate may be of doubtful value as a neutral buffer standard. Implicit reliance upon the purity and neutrality of a solution of the crystallized salt is certainly unjustifiable.

SOIL CHEMISTRY LABORATORY C. J. SCHOLLENBERGER
OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER, OHIO

RECEIVED MAY 24, 1932
PUBLISHED JUNE 6, 1932

AN ADDITION COMPOUND OF DIETHYLAMINE AND PHENYLBORIC ACID

Sir:

An addition compound has been prepared with diethylamine and phenylboric acid. It was expected that these should combine in a one to one ratio since boron trifluoride forms stable one to one addition compounds with ammonia or amines[1] and triphenylboron behaves in a similar manner.[2] Analyses, however, have shown that this substance contains three molecules of phenylboric acid to one of diethylamine.

This compound is readily prepared by allowing equal molal quantities[3] of the two substituents to react in anhydrous ether solution. There is a slight initial rise in temperature and after a few minutes a white solid (m. p. 85°) is precipitated. It is readily soluble in alcohol, acetone, benzene, chloroform, glacial acetic acid and dioxane, and sparingly soluble in diethyl ether, petroleum ether, water and carbon tetrachloride. When heated with water it decomposes, giving off diethylamine quantitatively.

The nitrogen content was obtained by heating the substance in dilute alkali and titrating the diethylamine which was volatilized with the vapors. It was observed that phenylboric acid could be titrated in the presence of glycerine just like boric acid itself, so the phenylboric acid (or possibly boric acid) residue in the Kjeldahl flasks was titrated in this manner. Independent boron analyses were obtained by heating the substance in bomb tubes with nitric acid, neutralizing the nitric acid to the methyl red end-point, and titrating the boric acid to the phenolphthalein end-point in the presence of glycerine.

Determination	Found, %		Calculated for $(C_6H_5B(OH)_2)_3 \cdot (C_2H_5)NH$, %
Nitrogen	3.20	3.18	3.19
Boron from residue of N_2 analysis	7.63	7.37	7.40
Boron, Carius determination	7.21	7.28	7.40

It should be pointed out that these analyses do not preclude the possibility that this compound may have lost one molecule of water. This work is being continued.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

G. E. K. BRANCH
DAVID L. YABROFF

RECEIVED MAY 25, 1932
PUBLISHED JUNE 6, 1932

[1] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, Vol. V, p. 122; Kraus and Brown, THIS JOURNAL, **51**, 2690 (1929).

[2] Stock and Zeidler, *Ber.*, **54**, 531 (1921); Krause, *ibid.*, **57**, 813 (1924).

[3] It was first prepared in this manner since the one to one addition compound was expected.

ALLYL ETHERS OF HETEROCYCLIC ENOLS

Sir:

During research carried out in connection with the preparation of substances allied in structure to the alkaloid coniine, it became necessary to study the preparation and pyrolysis of the allyl ethers of heterocyclic enols. It is well known that α- and γ-N-heterocyclic enols show a marked tautomeric mobility of the enolic hydrogen between oxygen and nitrogen with preferential attachment to the nitrogen. The O-ethers are more difficult to prepare than the N-ethers, the best yields of the former being obtained via the silver salts or chlorine substituted derivatives.

The alkoxy ethers on heating usually undergo a rearrangement of the alkyl group, which wanders invariably to the nitrogen atom in preference to a nuclear carbon atom. One might expect that the allyl group would undergo an analogous migration [*cf.* Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Company, 1929, pp. 205 and 223]. Tschitschibabin and Jeletsky [*Ber.*, **57**, 1158–61 (1924)] report having pyrolyzed O-allyl-carbostyril into the N-isomeride.

It has been found in the course of the present work that the migration of the allyl group can occur from oxygen to the adjacent β-unsaturated carbon atom. Thus 4-allyloxyquinaldine pyrolyzes almost quantitatively on heating for a short time, at 200°, to 3-allyl-4-hydroxyquinaldine, the constitution of which has been proved by its synthesis from α-allyl-β-phenylaminocrotonic ester. This is interesting since, in the case of 4-methoxyquinaldine, migration of the methyl group takes place to the nitrogen atom [Conrad and Limpach, *Ber.*, **20**, 956 (1887)].

The significance of these results, and of those obtained with other oxy-N-heterocyclic substances, will be reported shortly in greater detail.

DEPARTMENT OF ORGANIC CHEMISTRY
UNIVERSITY OF SYDNEY
SYDNEY, AUSTRALIA

BURNETT MANDER-JONES
VICTOR MARTIN TRIKOJUS

RECEIVED MAY 25, 1932
PUBLISHED JUNE 6, 1932

NEW BOOKS

Chemistry at the Centenary (1931) Meeting of the British Association for the Advancement of Science. W. Heffer and Sons, Ltd., Cambridge, England, 1932. Price, 7/6, net.

The experience of a century has taught scientists in general and chemists in particular to expect papers of interest and pronouncements of lasting importance at the meetings of the British Association. It is hard for us to say whether the attractively published volume before us, a complete record of the Proceedings of the Chemistry Section, contains any pronouncement of an epoch-making character, but it is easy to discover that every paper is an interesting account of some of the very latest work. A scholarly dis-

course on "Michael Faraday and the Theory of Electrolytic Conduction" by Sir Harold Hartley opens the Proceedings. It contains an excellent historical survey of the development of thought and experiment on solutions of ionized solutes. There follow discussions on "The Influence of the Medium on the Properties of Electrolytes" which in spite of much writing is still far from being a solved problem, "Vitamin-A and the Carotenoids," "The Chemistry of Vitamin-B and Related Problems" and "The Structure of Simple Molecules," and a symposium on "The British Fuel Problem."

In all these discussions the contributors, a truly international array of celebrities, have given consideration to the general scientific reader and as a result the very latest advances are presented most comprehensibly. The fearless and scientific way in which the coal and oil problems of Britain are treated makes the book worth buying for this symposium alone.

While this collection, containing, as it does, contributions not yet published elsewhere from authorities all over the world, will surely be of surpassing interest to those actively pursuing research in the subjects mentioned above, we heartily recommend it to those general readers who wish to keep themselves posted on the latest news from the front of these rapidly advancing lines of investigation.

R. E. GIBSON

Rechnenverfahren und Rechnenhilfsmittel mit Anwendungen auf die analytische Chemie. (Methods of Calculation, Aids to Calculation and Applications to Analytical Chemistry.) By Prof. Dr. OTTO LIESCHE, Seelze bei Hannover. Verlag von Ferdinand Enke, Stuttgart, Germany, 1932. viii + 203 pp. 24 figs. 16.5 × 25.5 cm. Price, RM. 20; bound, RM. 22.

There are innumerable manuals devoted to chemical arithmetic and there are many textbooks of higher mathematics particularly designed for the enlightenment of chemists. I am not acquainted with any book covering the important aspects of chemical computation discussed in this volume.

The initial chapter of fifty or more pages is devoted to methods of simple numerical computation, particularly multiplication and division. The author first points out that these subjects are usually taught us so early in our intellectual development that they cannot be presented at that time from the abstract point of view which is necessary both for their thorough comprehension and their most efficient use. Moreover, arithmetic in general and the simpler parts of algebra are neglected in our higher mathematical training so that their application to the most frequent computational requirements of our later work is frequently lost. The author thereupon gives an excellent presentation of the so-called Ferrol methods of multiplication and division, and in a form particularly adapted for self-instruction. Many of these rapid methods should, according to the author, greatly lessen the need of resorting to logarithms, etc.

The second chapter sets forth the utilization of the various aids to multiplication and division—namely, logarithms, slide-rules and calculating machines.

The third chapter discusses at length specifically chemical computations and their algebraic formulation, taking up simple gravimetric analysis, "indirect" analysis (utilizing determinants), analysis of complex mixtures, errors and computations dealing with gases. The final chapter discusses nomography.

This is certainly a most instructive book.

ARTHUR B. LAMB

The Preparation of Pure Inorganic Substances. By E. H. ARCHIBALD, Professor of Analytical Chemistry, University of British Columbia. John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1932. x + 383 pp. 14.5 × 22.5 cm., 20 figs. Price $3.75.

The guiding principle followed in the compilation of this work is clearly set forth in the opening paragraph of the Preface:

"The past thirty years have seen a marked advance in the precision and accuracy of physical and chemical, as well as other scientific measurements. In order to take advantage of these improvements, it is frequently necessary for the chemist to supply substances of a much higher degree of purity than corresponds to our "C. P." products. Fortunately, during these thirty years, many methods have been devised, and a great many principles have been set forth, according to which the purification of a large number of chemicals can be effected. What are thought to be the more dependable and simple of these methods are set forth in the following pages."

The author is eminently qualified to speak with authority upon this subject, by reason of his long contact with and his outstanding success in atomic weight determinations, which involve the preparation of materials approaching absolute purity and the careful elimination of errors in the use of such reagents. Many of the methods described have been followed with utmost care by the author and his associates and most of the others are familiar to him by reason of the close parallel in his own work. Such a setting gives the reader a justified confidence in the authority and integrity of the author.

Chapter 1 is devoted to a general discussion of the methods of purification and the refinements which may be employed in each. For example, crystallization is discussed in detail with respect to the effect of inclusion, adsorption, the solid solution of isomorphous substances, the size and form of the crystals, the percentage of the salt crystallizing out, and the efficiency of centrifugal drainage and washing. In addition, attention is paid to the danger of contamination from laboratory utensils of various sorts, and to the adsorption of gases. Each of the remaining sixteen chapters is devoted to a family of the Periodic Table, beginning with the Noble Gases and

concluding with Ruthenium, Palladium and Platinum. A few of the least important elements are not included, but the list includes seventy-three of the elements which are most frequently encountered. There are numerous quotations from original papers and the abundant references will be extremely useful in case additional detail is required. Both a subject index and an author index are included.

This book will be a valuable time saver for all chemists who are concerned with the preparation of pure inorganic compounds.

B. S. HOPKINS

A Course in Quantitative Analysis. By J. SAMUEL GUY, Professor of Chemistry, Emory University, and AUGUSTA SKEEN, Assistant Professor of Chemistry, Agnes Scott College. Ginn and Company, 15 Ashburton Place, Boston, Massachusetts, 1932. xiv + 242 pp. 14.5 × 21.5 cm. Price, $2.20.

This little volume covers an elementary course requiring only meager preparation in chemistry (or mathematics). Introducing volumetric studies first, eleven, well-assorted, approximately 0.1 *N* stock solutions are prepared and standardized, $H_2C_2O_4 \cdot 2H_2O$ being preferred as a primary standard because of its availability for titration with both sodium hydroxide and potassium permanganate. The other solutions are standardized directly or indirectly from these. Sixteen volumetric exercises are described, followed by five gravimetric determinations, the latter including water by loss on heating, copper by precipitation as cupric hydroxide and by electrolytic deposition, sulfate by precipitation, and carbon dioxide by loss in weight on dissolving in hydrochloric acid. Details are also given for the use of other primary standards (Fe, Na_2CO_3, NaCl, As_2O_3, and $Na_2C_2O_4$), for a number of optional gravimetric experiments, and for the colorimetric determination of hydrogen-ion concentration.

For the teacher who feels that the present courses are unwieldy, this book will prove refreshing in its simplicity. Unfortunately, however, in the attempt to simplify, the authors have failed rather frequently in scientific accuracy. The following cases will serve as illustrations: (1) two contradictory procedures are given for determining the resting point of a balance; (2) the need of boiling out carbon dioxide when titrating sodium carbonate with hydrochloric acid (using phenolphthalein as indicator) is discussed in terms of the reaction of carbonic acid with sodium chloride; (3) the electronic description of the reaction between potassium permanganate and ferrous sulfate (pp. 57–58) is obviously unsound.

On the whole, the student who completes a course based solely on this book will have become acquainted with a fair variety of quantitative manipulations, but he may fail to understand the errors of quantitative analyses or the way in which various procedures avoid them.

R. K. MCALPINE

The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals. By ALEXANDER NEWTON WINCHELL, Professor of Mineralogy and Petrology, University of Wisconsin. With a Chapter on the Universal Stage, by Richard Conrad Emmons, Associate Professor of Geology, University of Wisconsin. Second edition. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1931. xvii + 403 pp. Illustrated. 15 × 23.5 cm. Price, $5.00.

The appearance of this book marks an important step in the education of the chemical fraternity in the application of the methods developed by mineralogists for the description and identification of crystalline compounds. No one who has had an opportunity to make use of these methods can fail to be impressed with their power and convenience, and the rapidly increasing use of the petrographic microscope in research and industrial laboratories shows that they are appreciated. There has long been a need for a book containing optical data for artificial crystalline compounds, and also for a textbook of optical crystallography in English that would teach the fundamental principles and main facts, and the methods by which they are applied in the measurement and observation of crystallographic properties.

Winchell's book represents the most complete set of tables and synoptic data for artificial inorganic compounds thus far published and as such will be found valuable by all who use the polarizing microscope. This assemblage of crystallographic data constitutes Part II, while Part III comprises a well arranged set of determinative tables based thereon. In connection with Parts II and III the reviewers commend plate V as a useful chart classifying artificial inorganic solid substances on the basis of birefringence optic sign, and refringence.

The amount of critical judgment that it is fair to expect of an author of tables is difficult to fix. It should be noted, however, that Winchell himself states in the introduction that "the general rule in this book is to give the values of the indices of refraction of pure substances to the fourth decimal place and in three kinds of light (C, D and F).... The indices of refraction of some pure substances have not been measured with accuracy and accurate measures have not always been made on strictly pure material; in such cases the indices of refraction are given only to the second or third decimal place." This implies a critical discrimination that has not been carried out. In some cases inaccurate values have been given instead of accurate values well known in the literature (example: $CuSO_4 \cdot 5H_2O$). In other cases more than one set of values of the indices of a compound are given, all expressed to four places of decimals but differing among themselves in the third place (examples: $NaNO_3$, KNO_3, $NiSO_4 \cdot 7H_2O$, NH_4Cl). Refractive indices of numerous compounds are quoted to four places of decimals although the measurements were made by means of an indefinite series of wave lengths through colored screens; several of the values thus obtained are inaccurate in the third place owing to the high dispersions of

the compounds and the failure to use monochromatic light (examples: $Nd_2(MoO_4)_3$, $Ce_2(MoO_4)_3$, $CaWO_4$, $SrMoO_4$). Little or no attention has been given to recorded divergences of measurements, or to irregularities in the curves of dispersion or of optic axial angle, $2V$, such as are indicated in "International Critical Tables," Volume VII. The exercise of critical judgment is of course difficult and laborious and the reviewers do not state that the author of a table is bound to exercise it. They consider it necessary to point out, however, that the claim made by Winchell that he has exercised such judgment is not made good in his tables. Moreover, he has not taken advantage of careful critical work previously done.

Part I entitled "Principles and Methods" "consists in large part of revised selections from the author's 'Elements of Optical Mineralogy,' Part I, 3d Edition." It represents an attempt to give the reader an understanding or working knowledge of the methods whereby the data of Parts II and III have been obtained and are applied. The phenomena observed in crystals in convergent light are not discussed, however; Winchell refers the reader to his "Elements of Optical Mineralogy, Part I" (Chapters XIV and XVIII) for a treatment of this subject, which of course must be understood by all who intend seriously to use microscopic methods for the description and determination of crystalline compounds. The treatment of crystallographic principles and methods in Part I of "The Microscopic Characters of Artificial Minerals" is clearly set forth and well illustrated but contains some erroneous theoretical statements of matters now well established. These are discussed in detail in a forthcoming article in the *American Mineralogist.*

Chapter 2 (of Part I) discusses apparatus and preparation of material, and Chapter 3 (also of Part I) the optical properties of isotropic substances. Winchell uses the symbol N instead of the customary (in all or nearly all countries but France) n; in later chapters he also uses N_o, N_e and N_g, N_m and N_p for the indices of refraction of uniaxial and biaxial crystals, respectively. The use of the customary symbols n, ω, ϵ, γ, β, α, for refractive indices in the descriptive tables would have segmented the long lines of Roman type and eliminated the small subscripts adopted by the publisher, which are difficult to read.

The phenomena observed under the microscope with central illumination of powdered grains immersed in a liquid, sometimes called the "Becke line," are improperly so-called;[1] the expression, "Becke line," was coined by Salomon[2] to designate the phenomena associated with total reflection at a vertical interface, which differ in theoretical interpretation from the phenomena obtained with central illumination of irregular grains; the latter are properly known as the central illuminaton effect.

[1] *Cf.* F. E. Wright, *J. Wash. Acad. Sci.*, **5**, 104 (1915).

[2] W. Salomon, *Z. Kryst. Min.*, **26**, 182 (1896).

The prominence given the "double variation" method of determination of index of refraction, together with the failure to describe the usual methods adequately, is a serious shortcoming. The ease in application of the usual methods, which has already been proved in many places and by many workers, warrants their careful description in a book of this character. The majority of measurements of indices of refraction are made for the purpose of the identification of the substance and the greater speed and convenience of the simplest immersion method make it the unquestionable choice in nearly all determinative work. In measuring refractive indices for record it is desirable to obtain them with an accuracy of ± 0.001 or better, which can be accomplished by the usual methods or by the variation of the wave length in the dispersion method or by the variation of both wave length and temperature in the double variation universal stage method of Emmons. Incidentally, it should be noted that the methods called by Winchell "immersion," "single variation" and "double variation" methods are all immersion methods.

Winchell's statement (p. 65): "The technique of measuring indices of refraction by this [dispersion] method is the same as that involved in using the double variation method with the single exception that all measures are made at room temperature...." is hardly justified by the facts; the reviewers would say that the technique required in the double variation method is more complicated. Although Winchell does not claim that the double variation method is superior in point of accuracy to the dispersion method, he does state that the double variation method is more convenient. On this question there is difference of opinion. Attention should be called to the fact that a very important sacrifice, recognized as a disadvantage by Winchell's collaborator, Emmons, is made in securing the ability to vary the temperature over a range by means of Emmons' apparatus. The variation of temperature is accomplished by means of a water cell between the condenser and the preparation and according to Emmons[3] this makes it impossible to obtain interference figures in convergent light from the grains the refractive indices of which are being measured. Without the possibility of using the conoscope (convergent light) to obtain interference figures and unless the universal stage is used, it is impossible to recognize optic normal grains. Now in all cases it is highly desirable to supplement the purely statistical method of determining α and γ (n_p and n_g) by checking the orientations of the grains believed to exhibit α and γ. If the mineral has no cleavage, α and γ can be obtained by the purely statistical method, but one is never sure even in this case that the lowest index, α, and the highest index, γ, have really been obtained unless the orientations of the grains are established. In cases of minerals with good cleavage the statistical method is unreliable and the student or investigator who relies

[3] R. C. Emmons, *Am. Min.*, **14**, 425 (1929).

upon it exclusively in such cases will come to grief sooner or later. The orientation of the grain believed to exhibit the minimum or maximum index can be established, either by means of its interference figure in the dispersion method or by the use of the universal stage in the double variation method as described by Emmons. In the dispersion method the establishment of the orientation of the grain by means of its interference figure involves merely the removal of the eyepiece and a glance down the tube, or if the grain is small the use of one of the numerous special eyepieces available for this purpose. It is to be noted that finer grains can be handled accurately by the dispersion method than by the double variation universal stage method of Emmons, an important point in the study of artificial materials, which are so often obtained only in a fine-grained condition. Interference figures can be obtained from grains 0.005 mm. in diameter in many cases and 0.01 mm. in nearly all cases in the dispersion method; in the double variation method Emmons[4] claims that grains as small as 0.03 mm. in diameter can be handled with the universal stage.

This review may be summarized and concluded with the statement that the book contains a very valuable collection of optical and geometrical crystallographic properties to which has been added a rather unsatisfactory account of selected aspects of optical crystallography.

[4] R. C. Emmons, *Am. Min.*, **16**, 554 (1931).

GEORGE TUNELL
GEORGE W. MOREY

The Structure and Composition of Foods. Vol. I. Cereals, Starch, Oil Seeds, Nuts, Oils, Forage Plants. By ANDREW L. WINTON, Ph.D., and KATE BARBER WINTON, Ph.D. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. 710 pp. 274 figs. 15.5 × 23.5 cm. Price, $8.50.

This is a unique and convenient book. It combines a description of the macroscopic and microscopic structure of cereals, nuts, oil seeds and forage plants, with a discussion of their composition. The latter includes not only the results of the conventional proximate analysis, but the products of hydrolysis of the native proteins, physical and chemical constants of the fats and other organic constituents, composition of the ash, and the nature of the enzymes present as well, when such data are available in the literature. In numerous instances the authors have also described manufactures based on these materials and the fractionation of the constituents of the original seed or fruit into the several commercial products. Thus one secures a rather detailed physical and chemical "picture" of these food and forage plants. Of course, the authors cannot trace the chemical technology of the 173 or more materials in as much detail as is attempted in manuals dealing with a limited group or a single fruit or seed. One cannot but be impressed by the volume of useful information recorded on the

seven hundred pages of this book, however, and also by the care and discretion exercised in its selection from the mass of data in the literature.

The structures of the individual forage grasses are not detailed in Part III, although the histology of timothy stems and leaves is shown in three plates. Discussion of the composition of these forage grasses is confined to proximate analyses. The value of the forage plant section might have been enhanced by the inclusion of some reference to cyanogenetic glucosides and the conditions attendant upon their appearance in the forage in lethal concentrations.

Taxonomists may not agree with the Wintons' inclusion of buckwheat, chestnuts, legumes and various weed seeds with the "cereals"; in fact the titles used in this connection are somewhat confusing to the extent that the book contains material which might not be expected to be present. The reviewer feels that the section dealing with the chemical nature of starch would be strengthened by the inclusion of a brief summary of the views of Samec, Haworth and Irvine. The inference that endosperm and pericarp of the cereal grains are essentially devoid of fat, which might be drawn from the first sentence under fats, on page 61, is hardly supported by certain critical studies.

The book cannot fail to be of great service to food chemists and others who desire to learn how these groups of foods are constituted structurally and chemically. The other two volumes in this series are anticipated with interest.

C. H. BAILEY

Glastechnische Tabellen. Physikalische und chemische Konstanten der Gläser. (Glass Tables. The Physical and Chemical Constants of Glasses.) Edited by DR. WILHELM EITEL, DR. MARCELLO PIRANI and DR. KARL SCHEEL. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1932. xii + 714 pp. Illustrated. 20 × 28.5 cm. Price, RM. 145; bound, RM. 149.80.

This vast compendium of technical tables on glass is like the Landolt–Börnstein Physikalisch-chemische Tabellen. It has been made possible through the subsidy of the Deutsche Glastechnische Gesellschaft, the editors named above and their associates.

It is divided into three parts. Section 1 covers equilibria in glass-forming systems, conditions under which they may best function, the proportions of the components and their crystalline phases. It takes up the glass-forming oxides, borate systems, carbonate systems, phosphate systems and silicates. Space is then devoted to two, three and four, or more, component systems as well as to organic substances which may enter a glassy state. This section is replete with phase diagrams which indicate the particular substances possible under various conditions and the point at which eutectic mixtures result. The crystal forms which are obtained are generously illustrated. Section 1 covers the first 88 pages.

Section 2 is devoted to physical and chemical constants such as viscosity, surface tension, internal strain, tensile strength, softening point, specific gravity, coefficient of elasticity, compressibility, cohesion, hardness, refractoriness, porosity to gases, adsorption and evolution of gases, thermal expansion, specific heat, heat conductivity, dielectric constants, electrical capacity, electrical conductivity, sparking point, potential differences, magnetic susceptibility, crushing strength, photo-elasticity, effect of electric fields on refraction, spectral transmission, ultraviolet transmission, infra-red transmission, total light transmission, properties of light filters, dispersion data, chemical susceptibility with methods of testing and results, devitrification. 536 pages are covered by this section, which not only contains numberless tables and diagrams but copious references to the literature covering every item discussed. Here, every glass has a key number which refers to some part of Section 3 of the publication.

Section 3 contains a systematic record of the chemical composition of the glasses covered in Section 2. These are the alkali silicates; the alkali-lime silicates, containing up to 1% of alumina; the alkali-lime-alumina silicates; the alkali silicates with those of calcium, magnesium, strontium, barium, iron, manganese and aluminum; the alkali-alkaline-earth-alumina-lead silicates; the alkali-alkaline-earth-boro silicates; glasses both clear and clouded containing the halogens and phosphorus; silica-free glasses like the borates, phosphates and arsenates; glassy organic substances. With each analysis there is not only a key number but a reference to pages in Sections 1 and 2, where the particular glasses are discussed as to their properties. Section 3 covers 83 pages.

This gigantic undertaking is priceless. The type is clear, the diagrams and illustrations are clean-cut, the cross references are well ordered and the reviewer has thus far not found a single fault in the use of such references. Here is a compilation of data never before available to glass technologists and scientists in other fields who are interested in the properties of glass. It should prove indispensable to serious workers in the field. There is a good table of contents, but the index might be more complete.

The authors and their collaborators are certainly to be congratulated for having made a precious contribution. It is to be hoped that these tables may be translated into English and thus made available for those who are unable to use the German publication.

ALEXANDER SILVERMAN

The Glycosides. By E. F. ARMSTRONG, D.Sc., Ph.D., LL.D., F.R.S., and K. F. ARMSTRONG, B.A., B.Sc. Longmans, Green and Co., 55 Fifth Ave., New York, 1931. vii + 123 pp. 15.5 × 25 cm. Price, $4.25.

An earlier monograph by E. F. Armstrong in the series of Monographs on Biochemistry edited by R. H. A. Plimmer and F. G. Hopkins bears the

title, "The Simple Carbohydrates and the Glucosides." Since the date of publication of the last edition, the activity of chemists in the field of sugars as well as in the field of glycosides (the newly-accepted term) has been greater than in any other field of organic chemistry, so that the division of the material into two separate monographs is very natural, particularly for the reason that to many workers in the field of glycosides the chief interest lies in the chemistry of the aglucones. Indeed, the work of Willstätter on anthocyanin glycosides, which has been continued by Robinson and his associates, and the investigations of Jacobs and of Windaus on cardiac glycosides—which will remain of outstanding interest to organic chemists—are concerned principally with the structure of the aglucones.

The new monograph on glycosides, which introduces to the chemical world the third generation of Armstrongs, should be regarded as a brief summary of the more recent work on natural and synthetic glycosides rather than as an exhaustive treatise on the subject. The authors emphasize that "no attempt has been made to do more than list the various glycosides and indicate their structure and relationships." In this manner are discussed glycosides containing the following aglucones (should it not be aglycones?)—phenols, hydroxyanthraquinones, hydroxycoumarins, anthoxanthins and anthocyanins, cardiac aglucones, glycosides of mustard oils, cyanophoric glycosides, nucleosides, indican and pentosides. This list of glycosides is a striking illustration of the heterogeneity of the substances capable of coupling with sugars and of the difficulty in correlating all glycosides on a rational genetic basis. Yet the work of recent years has aimed at a chemical correlation of certain groups of glycosides, if not of all, and much success has been attained in this respect in the glycosides of anthoxanthin and anthocyanin groups and perhaps even more so in the group of the cardiac glycosides. The idea of genetic relationship of the components of glycosides, of the sugars and of the aglucones runs through every chapter dealing with the natural glycosides as the basic pattern unifying the heterogeneous material.

In Chapter II of the book, which is the first chapter devoted to natural glycosides, the authors write:

> In time the facts available may make it possible to explain the progressive building up of more complicated aglucones and correlate these perhaps with species or plant habitat. With so few primary materials available, with carbon dioxide as its sole source of carbon, it is an unending source of wonder that the plant has created an apparently limitless range of organic compounds, sometimes of fantastic complexity.

In subsequent chapters, again and again the thought is advanced that the anthoxanthin and the anthocyanin, the aglucones and the phenolic aglucones may have their origin in a common hexose (namely, glucose) and in some cases, in hexoses and trioses. The reviewer would hesitate to attribute to Nature this very inefficient way of operating, yet he must admit

that from a literary and didactic viewpoint, the thought serves a useful purpose.

Another expedient used by the authors to unify the heterogeneous material is the frequent reference to the biological aspects of the glycosides. Among them some are important from a practical viewpoint and may be of little familiarity to the organic chemist; for instance, the method of diagnosing sugars by the inhibition method, which is based on the fact that an enzyme specific for a certain glycoside is inhibited in its activity only by the sugar that enters into the structure of the glycoside. Of all natural glycosides those of anthoxanthins and anthocyanins are discussed in greater detail.

Only a few inaccuracies came to the attention of the reviewer. Two may be mentioned. Referring to digitalis glycosides, the authors attribute the activity of the glycoside to the unsaturated lactone group and later in the same chapter, reviewing the properties of the strophanthus glycosides, they state that the activity of the entire molecule is enhanced by the unsaturation of the lactone group. The latter statement is correct and applies to all the cardiac glycosides. The first statement was for a time the generally-accepted one but it has been abandoned. In speaking of nucleosides, the authors state that ribose and desoxyribose nucleosides can be prepared by the identical hydrolytic agents. This is not correct inasmuch as the desoxyribose nucleosides are at present obtainable only through the action of enzymes. The emphasis of the authors on the probability of the formation of *d*-ribose from xylosephosphoric acid seems to the reviewer exaggerated inasmuch as the author of the suggestion, Robinson, viewed it in the light of a mere possibility to be borne in mind—a possibility which thus far has no experimental evidence in its favor.

In addition to the chapters on natural glycosides, the monograph contains an introductory chapter dealing with definitions of the terminology, with the theories of the origin of hexoses, with theories aiming to explain the prevalence of glucose as compared with other hexoses, with speculations on the transformation of hexoses into inositols and into polyhydroxyphenols and with the general properties of glycosides.

The chapters on synthetic glycosides, on uronic acids, on the function of glycosides in plants and on the utilization of carbohydrates in plants, containing a discussion on ripening of fruit, are very brief and rather incomplete.

The monograph will be read with great benefit by all not yet acquainted with the chemistry of natural glycosides.

P. A. LEVENE

BOOKS RECEIVED

April 15, 1932–May 15, 1932

WILLIAM C. BRAY AND WENDELL M. LATIMER. "A Course in General Chemistry." Revised edition. The Macmillan Company, 60 Fifth Ave., New York. 159 pp. $1.60.

STUART R. BRINKLEY. "Introductory General Chemistry." The Macmillan Company, 60 Fifth Ave., New York. 565 pp. $3.00.

J. DAVIDSOHN AND K. RIETZ. "Fettberichte. Gesamtübersicht über das Gebiet der Fette, Fetteprodukte und verwandten Stoffe für 1927, 1928, 1929, 1930." Verlag von Ferdinand Enke, Stuttgart, Germany. 458 pp. RM. 47; bound, RM. 49.

C. DRUCKER AND A. FINKELSTEIN. "Galvanische Elemente und Akkumulatoren. Darstellung der Theorie und Technik nebst Patentregister." Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 426 pp. M. 34; bound, M. 36.

HENRY GILMAN, Editor-in-Chief. "Organic Syntheses. Collective Volume I." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 564 pp. $6.00.

JOEL H. HILDEBRAND. "Principles of Chemistry." Third edition. The Macmillan Company, 60 Fifth Ave., New York. 328 pp. $2.25.

E. L. LEDERER. "Kolloidchemie der Seifen." Verlagsbuchhandlung Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 430 pp. RM. 38; bound, RM. 39.80.

ALEXANDER LOWY AND BENJAMIN HARROW. "An Introduction to Organic Chemistry." Third edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 412 pp. $3.00.

A. MITTASCH AND E. THEIS. "Von Davy und Döbereiner bis Deacon, ein halbes Jahrhundert Grenzflächenkatalyse." Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 279 pp. Mk. 18.50.

J. H. VAN VLECK. "The Theory of Electric and Magnetic Susceptibilities." Oxford University Press, 114 Fifth Ave., New York. 384 pp. $7.50.

"Annual Reports on the Progress of Chemistry for 1931." Published by The Chemical Society, Burlington House, Piccadilly, London, W. 1, England. 10/6, net; postage, 6d.

The Journal of the American Chemical Society

VOL. 54 JULY, 1932 No. 7

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND WASHINGTON UNIVERSITY]

THE CRYSTAL STRUCTURES OF ELECTRODEPOSITED ALLOYS. AN X-RAY DIFFRACTION STUDY OF SILVER–CADMIUM DEPOSITS[1]

BY CHARLES W. STILLWELL AND LAWRENCE E. STOUT

RECEIVED NOVEMBER 20, 1931 PUBLISHED JULY 6, 1932

The electrodeposition of alloys is a comparatively recent development. The number of binary alloys which may be successfully electroplated has increased greatly during the last few years due to a realization of their many practical applications. Very little is known of the structure of these alloys, however, since in all phase rule studies of binary alloys the system is usually in equilibrium when the several phases are identified. These results cannot be applied to electrodeposited alloys, since the latter are probably not in equilibrium. An x-ray diffraction study of electrolytic brass made some years ago[2] proved that under specified conditions a true α-phase is deposited, a solid solution rather than a mixture of the metals. Recently several rather superficial papers have been published[3] giving diffraction data for the electrodeposited alloys: Cd–Ag, Cu–Zn, Cd–Sn, Cd–Ni. The only definite conclusion drawn is that the plate is not a mixture of the two metals, but contains compounds or solid solutions. The compounds are not identified, nor has any one of the binary alloys been systematically studied.

There are several variables which might influence the structure of an electrodeposited alloy. Among these are: (1) the composition of the plate, (2) the current density, (3) the temperature of deposition, (4) the rate of stirring and (5) the nature of the base metal. The aim of the present investigation of electrodeposited silver–cadmium alloys has been to study systematically by means of x-ray diffraction data the relation between the composition and the crystal structure of the plates. All deposits

[1] This paper was presented at the Buffalo meeting of the American Chemical Society, September, 1931.

[2] Nakamura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **2**, 287 (1925).

[3] Roux and Cournot, *Ind. élect*, **37**, 455 (1928); *Compt. rend.*, **186**, 1733 (1928); *Rev. mét.*, **26**, 655 (1929).

have been prepared at constant temperature and constant current density without stirring, and the effect of these other variables will be studied later.

Experimental

Some of the deposits investigated were prepared and analyzed by Stout at Washington University. Chemical analyses and the x-ray diffraction studies of all the plates were made at the University of Illinois. The baths from which the alloys were deposited were made as described by Stout and Thummel.[4] The alloy was deposited on sheet copper, 10 × 2 cm. and 0.1 cm. in thickness. Two duriron anodes were used, the cathode being adjusted between them and equidistant from each. The deposits were made at room temperature (27°) using a current density of one ampere per square decimeter. Three plates were prepared for each composition studied. In each case the first and third were analyzed and the second was used to determine the diffraction data. The equilibrium diagram for the silver–cadmium system has been studied by x-ray diffraction methods by several investigators[5] and the compositions of the alloys which were electroplated were chosen after a consideration of these equilibrium data.

The composition of the plates was determined by precipitating silver as silver chloride, removing the copper electrolytically from an acid solution and precipitating cadmium electrolytically from a basic cyanide solution.[6] The composition of the edge of a plate is different from that of the center. The center area was the portion analyzed in each case since the x-ray diffraction pattern was obtained from this area.

The relation between the composition of the bath and the composition of the deposit is shown in Table I.

TABLE I[7]

Silver in bath, %	9.1	12.0	23.1	25.9	41.2
Silver in deposit, %	18.5	23.4	47.4	52.0	69.0

The x-ray diffraction data were obtained by the powder method, using the General Electric multiple apparatus and a Coolidge tube with a

[4] Stout and Thummel, *Trans. Electrochem. Soc.*, **59**, 337 (1931).

[5] (a) Astrand and Westgren, *Z. anorg. allgem. Chem.*, **175**, 90 (1928); (b) Natta and Freri, *Atti. accad. Lincei*, [6] **6**, 422, 505 (1927); **7**, 406 (1928); *J. Inst. Metals*, **39**, 537 (1928); **40**, 573 (1928).

[6] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, pp. 197, 205.

[7] These values do not agree with those of Stout and Thummel.[4] The values in Table I have been checked independently by the present authors. The errors in the earlier values will be corrected in a publication by Stout soon to appear.

The relations between the crystal structures and compositions of the deposits, set forth in a previous note [Stillwell, THIS JOURNAL, **53**, 2416 (1931)] are invalidated by this revision of the chemical analyses of the deposits. The conclusions drawn in the note were based on the earlier data of Stout and Thummel.

molybdenum target. A firmly adhering electrodeposited layer may be very conveniently handled by this method. The copper strip on which the alloy was deposited was cut to a convenient size and bent through an angle of 180°, the radius of curvature of the outer plated surface being about 2.0 mm. Mounted properly at the center of curvature of the quadrant cassette, this affords a sharply curved surface from which the x-rays are reflected. The specimen is thick enough to prevent transmission of the x-ray beam, so that the lines of the resulting diffraction pattern are clearly defined and as narrow as it is possible to get them. The length of exposure is cut to a minimum under these conditions. Good patterns of a homogeneous deposit were obtained in fifteen to twenty hours with 20 m. a. It is convenient to reflect the radiation from a curved surface for another reason. When metals are electrodeposited, the crystals often assume a preferred orientation in respect to the base metal. If the orientation is sufficiently regular many of the planes of the crystal would not be in the proper position to diffract the x-rays and the pattern would be incomplete and more difficult to identify. In using a curved specimen, although the crystals may be oriented with respect to the base metal, there is sufficient variation in their orientation with respect to the x-ray beam to permit reflection from many more planes.

The alloy deposit was thin enough in every case to permit diffraction of the x-rays by the copper base, and the diffraction pattern for copper which was present in every film was used as a reference in measuring the patterns of the alloy phases, affording much greater accuracy than would otherwise be possible.

Analysis of Data

The diffraction data for the ten different alloys examined have been recorded and analyzed. The general procedure is illustrated in Table II for alloy 82.0% cadmium. The others were analyzed in the same way. The composition of the alloy is expressed in atomic per cent. of cadmium. The interplanar spacings, in Ångström units, are in the first column. The intensity of the lines was estimated as very strong (vs), strong (s), medium (m), weak (w) or very weak (vw). The lines of the copper pattern used as a calibration are designated "Cu." All of the alloys proved to be heterogeneous and the identifications of the several different crystalline phases are included in the table.

The accuracy with which the size of the unit cell may be determined from films obtained by this method is limited. The maximum probable error for the determination of the values of a_0 in the several phases has been estimated in the following way. As different values of the constant are tried in the $\sin^2\theta$ equation, the difference between constants may be reduced to the point where the calculated values for two successive constants

TABLE II

INTERPLANAR SPACINGS FOR ALLOY NO. 14 — 82.0 PER CENT. Cd. IDENTIFICATION OF THE ϵ, β', γ AND η PHASES IN THE ALLOY

		The ϵ-phase			The β'-phase			The γ-phase			The η-phase		
		$\sin^2\theta$			$\sin^2\theta$			$\sin^2\theta$			$\sin^2\theta$		
d_{hkl}	Intensity	Obs.	Calcd.	hkl	Obs.	Calcd.	hkl	Obs.	Calcd.	hkl	Obs.	Calcd.	hkl
2.67	s	0.0177	0.0177	100				0.0177	0.0178	321			
2.57	m										0.0191	0.0188	100
2.40	w	.0219	.0218	002	0.0219	0.0218	002						
2.33	vs	.0232	.0231	101				.0232	.0229	411	.0232	.0230	101
2.28	w				.0242	.0241	101						
2.08	s(Cu)												
2.03	vw							.0306	.0307	422			
1.885	w										.0355	.0356	102
1.802	m(Cu)												
1.785	s	.0396	.0395	102									
1.575	vw							.0507	.0507	620			
1.540	vs	.0532	.0531	110				.0532	.0533	541			
1.501	w				.0559	.0559	110	.0559	.0560	622	.0559	.0564	110
1.490	m										.0567	.0564	103
1.462	vw							.0589	.0585	631			
1.433	vw				.0613	.0613	111	.0613	.0611	444			
1.407	vw							.0637	.0637	543 550 710			
1.375	m	.0666	.0667	103									
1.335	w	.0708	.0708	200				.0708	.0711	642			
1.306	w				.0739	.0744	200	.0739	.0738	730	.0739	.0732	112
1.295	vs	.0750	.0749	112									
1.272	m(Cu)				.0778	.0777	112						
1.254	m				.0800	.0798	201				.0800	.0790	201
1.225	vw							.0840	.0838	554 741 811			
1.201	vw	.0873	.0872	004	.0873	.0872	004						
1.167	m	.0926	.0926	202							.0926	.0920	202
1.093	vw	.1052	.1049	104									
1.087	m(Cu)				.1062	.1058	104						
1.055	w										.1130	.1130	203
1.042	w(Cu)												
1.025	m	.1200	.1198	203									
1.010	w	.1238	.1239	210	.1238	.1234	203				.1238	.1236	114
0.988	s	.1291	.1293	211									
.958	w												
.947	m	.1405	.1403	114									
.932	mm	.1452	.1457	212									
.920	w										.1485	.1485	212
.892	w	.1588	.1584	204									
.862	w										.1696	.1694	213
.855	s				.1728	.1726	301				.1728	.1734	301
.837	m				.1799	.1792	213						
.828	m(Cu)												
.817	vw	.1892	.1893	115									
.807	m(Cu)												
.802	vw	.1960	.1960	006									
.781	w	.2067	.2070	205							.2070	.2070	303
.773	m				.2103	.2106	205						
.737	m(Cu)										.2320	.2317	215
.716	w				.2453	.2450	222				.2453	.2445	310
.712	w										.2486	.2487	311
.697	m	.2594	.2604	215									
.694	m(Cu)	.2617	.2614	223							.2617	.2613	312
.673	w	.2783	.2791	313									
.662	vw										.2880	.2878	108

TABLE II (*Concluded*)

		The ϵ-phase			The β'-phase			The γ-phase			The η-phase		
		$\sin^2\theta$			$\sin^2\theta$			$\sin^2\theta$			$\sin^2\theta$		
d_{hkl}	Intensity	Obs.	Calcd.	hkl	Obs.	Calcd.	hkl	Obs.	Calcd.	hkl	Obs.	Calcd.	hkl
0.650	w	0.2983	0.2996	224	0.2983	0.2975	400						
.638	w(Cu)												
.632	vw	.3165	.3173	314							0.3165	0.3170	402
.617	w												
.609	m	.3398	.3382	320									
.601	w	.3489	.3486	225	.3489	.3490	314						
.587	w	.3657	.3663	315									

ϵ-phase $\sin^2\theta = 0.0177\,(h^2 + k^2 + hk) + 0.00545\,(l)^2$
$a = 3.081 \pm 0.004$
$c = 4.81$

β'-phase $\sin^2\theta = 0.0186\,(h^2 + k^2 + hk) + 0.00545\,(l)^2$
$a = 3.006 \pm 0.004$
$c = 4.81$

γ-phase $\sin\theta = 0.001275\,(h^2 + k^2 + l^2)$
$a = 9.936 \pm 0.025$

η-phase $\sin^2\theta = 0.0187\,(h^2 + k^2 + hk) + 0.0042\,(l)^2$
$a = 2.998 \pm 0.004$
$c = 5.49$

satisfy the experimental values equally well, but constants greater or smaller than these two are unsatisfactory. At this point the values for a_0 have been calculated from each of these constants, the mean value of the constants has been used in the equation, and the error of the determination is indicated as plus or minus half the difference between the values of a_0 originally computed. For example, the experimental values for the β'-phase in alloy 82.0 (Table II) are satisfied equally well by values calculated from the constants 0.01855 and 0.01865, but are not satisfied by values from constants 0.01850 or 0.01870. The values of a_0 calculated from the accepted constants are 3.010 Å. and 3.002 Å., respectively. The constant used in the final equation is 0.0186, the value of $a_0 = 3.006 \pm 0.004$ Å. It is believed that this method of expressing the error gives a true picture of the degree of accuracy of the results. Since the purpose of this study is merely to identify the several phases present, great accuracy is not demanded in most cases. In connection with the discussion below, however, it is desirable to know as nearly as possible the values of a_0 for the β'-phase, and the limit of error on this phase has been carefully estimated.

The analyses of the specimens should be considered in the light of the following factors.

1. The multiplicity of phases and reflecting planes recorded in each pattern leads to the possible superposition of important lines of one phase on those of another. Thus in some cases it may be said that a certain phase may be present, but is not necessarily so, if the positions which would be taken by all of its important diffraction lines are already occupied by lines identified with other patterns. A weak pattern for the β-phase in particular may be obscured by the γ-phase pattern.

2. A consideration of relative intensities cannot be used in establishing

the presence or absence of the pattern of a phase, since some, and possibly all, of the crystalline phases are deposited in a preferred orientation with respect to the base metal. Although this difficulty has been minimized by curving the specimens, the intensities are still abnormal, as may be seen by a casual examination of the intensities of the reflections from the more important planes of the ϵ-phase in the several specimens. A direct comparison of the films brings out these abnormal intensities most strikingly.

3. It should also be noted that some evidence points to an apparently non-uniform distribution of the phases over the surface of the electrode. Of several specimens chosen from the same plate (82.0% cadmium) some give only the pattern of the ϵ-phase even after long exposure, while others show in addition the patterns of the other phases.

4. There is a minimum concentration for each phase, below which it cannot be detected by this method. This concentration will depend to a considerable extent on the thickness of the deposit. In general, the weight of alloy deposited on the plates used for this investigation was about 0.3 g. If thicker deposits were made, smaller concentrations of the several phases could be detected.

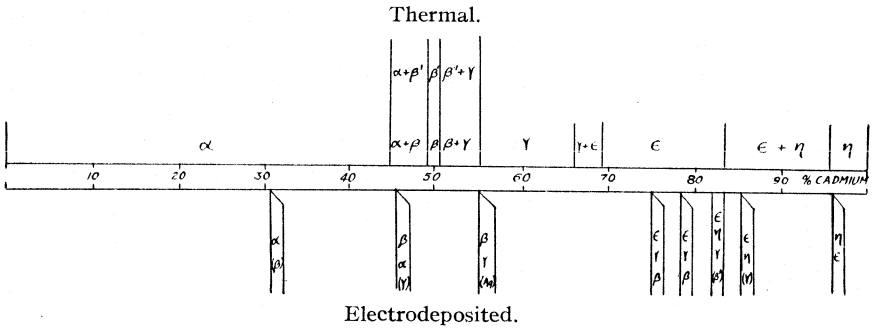


Fig. 1.—A comparison of the composition ranges of the several phases of the thermal silver–cadmium alloys with those of the same phases in the electrodeposited alloys.

The conclusions drawn from the several analyses are assembled in Table III and Fig. 1. For convenience the phases identified in the electrodeposited alloy are compared with those found by Astrand and Westgren[5a] in the thermal alloys of corresponding composition. The η-phase has the close-packed hexagonal structure—a solid solution of silver in cadmium. The ϵ-phase ($AgCd_3$) is also close-packed hexagonal, but of a different axial ratio. The γ-phase ($4Ag_5Cd_8$) is body-centered cubic, containing fifty-two atoms in the unit cell. The β-phase (AgCd) is of the cesium chloride type; while the α-phase is face-centered cubic, a solid solution of cadmium in silver. The β'-phase is metastable at room temperature for the compositions indicated. It is more fully discussed below. In each case the phase which predominates in the electrodeposited alloy is placed nearest

TABLE III

THE STRUCTURE OF SILVER–CADMIUM ALLOYS

Diffraction lines on film				Electrodeposited			Atomic per cent of cadmium	Thermal[15a]		
						$a = 3.090$	$a = 2.988$		η $a = 2.986$	
20					ϵ	$c = 4.81$	η $c = 5.49$	96.0	$c = 5.49$	(ϵ)
						10(8)	11(9)			
				(γ)	$a = 9.93$	$a = 2.998$	$a = 3.081$		ϵ $a = 3.091$	
27					5(2)	η $c = 5.49$	ϵ $c = 4.81$	85.0	$c = 4.81$	(η)
						9(4)	15(11)			
		$a = 3.006$	γ	$a = 9.93$		$a = 2.998$	$a = 3.081$		ϵ $a = 3.086$	
56		(β') $c = 4.81$		12(4)	η	$c = 5.49$	ϵ $c = 4.81$	83.0	$c = 4.81$	
						17(6)	26(16)			
		$a = 3.006$	γ	$a = 9.93$		$a = 2.998$	$a = 3.081$		ϵ $a = 3.084$	
56		(β') $c = 4.81$		12(5)	η	$c = 5.49$	ϵ $c = 4.81$	82.0	$c = 4.81$	
		13(2)				20(7)	27(16)			
			β	$a = 3.325$	γ	$a = 9.93$	$a = 3.047$		ϵ $a = 3.070$	
32				4(2)		7(5)	ϵ $c = 4.81$	78.0	$c = 4.81$	
							16(16)			
			β	$a = 3.325$	γ	$a = 9.93$	$a = 3.047$		ϵ $a = 3.060$	
35				7(3)		12(7)	ϵ $c = 4.81$	75.0	$c = 4.81$	
							19(18)			
	$a = 2.99$	$a = 3.006$	(Ag)	$a = 4.068$	γ	$a = 9.93$	β $a = 3.325$			
29	(β') $c = 4.81$	(β') $c = 4.81$		9(2)		19(11)	11(6)	55.0	γ $a = 9.935$	β $a = 3.327$ β' $a = 2.989$
	7(0)	8(0)								$c = 4.81$
	$a = 3.006$	$a = 3.047$	γ	$a = 9.93$	α	$a = 4.16$–	β $a = 3.325$			β' $a = 2.973$
37	(β') $c = 4.81$	(ϵ) $c = 4.81$		10(2)		4.17	12(4)	46.0	α $a = 4.175$	β $a = 3.323$ $c = 4.81$
	7(0)	7(2)				12(1)[a]				
							α $a = 4.12$–			
21					(β)	$a = 3.32$	4.16	31.0	α $a = 4.145$	
						2(1)	15(11)			

[a] The intensity of most of these twelve lines shows conclusively that the α-phase is present.

the center of the dividing line between thermal and electrodeposited alloys. This order is observed in both table and figure. After the most predominant phase has been recorded, the order of the other phases listed is usually arbitrary, since their relative concentrations cannot be accurately estimated. Column 1 lists the total number of lines measured on each film. The figure beneath each phase designates the number of lines on a particular film which may indicate the presence of this phase. The figure in parentheses is the number of lines which indicate only this phase and can belong to no other phase. The presence of most of the phases listed is definitely indicated by the diffraction patterns. The phases which may or may not be present, when considered in the light of diffraction data, are listed in parentheses.

Discussion

The β'-Phase.—Astrand and Westgren[5a] have obtained the β'-phase by heating the β-phase for five to ten hours just below 460°. The β'-phase is recorded in Table III in such a way as to indicate that it is a phase, stable at higher temperatures over the range of composition occupied by the β-phase at room temperature. The β'-phase has the close-packed hexagonal structure and the same axial ratio as the ϵ-phase, differing from the latter only in the size of the unit cell. Moreover, the magnitude of this difference in the size of the unit cell suggests that the β'-phase is a continuation of the ϵ-phase; that the ϵ-phase at the higher temperature extends over the range of composition occupied by the β- and γ-phases at room temperature. This is the interpretation suggested by Astrand and Westgren. If it be the correct one it should be possible to heat and quench the γ-phase and prepare a metastable close-packed hexagonal phase in which the value of a_0 lies between 2.989 Å. (the upper limit for the metastable $\beta'(\epsilon)$) and 3.040 Å. (the lower limit for the stable ϵ-phase). Astrand and Westgren were unable to do this. Natta and Freri[5b] claim to have prepared a $\beta'(\epsilon)$ phase in which $a_0 = 3.01$ Å., leaving a gap only from $a_0 = 3.01$ Å. to $a_0 = 3.04$ Å. Since electrodeposition seems to be a good method for the preparation of metastable metals, it was hoped that this gap between $a_0 = 3.04$ for the ϵ-phase and $a_0 = 3.01$ Å. for the $\beta'(\epsilon)$ phase might be closed. As may be seen from the data, however, no close-packed hexagonal lattice with a value of a_0 between these two has been identified in any of the specimens.

It is questionable whether the $\beta'(\epsilon)$ phase is deposited at all under the conditions of the experiment. There is no positive evidence of a $\beta'(\epsilon)$ lattice on the patterns for plates of 55 and 49% cadmium where it should naturally occur. The possibility of its presence in these plates is indicated in Table III. The most evidence in its favor exists in the pattern analyzed in Table II. Even here there are only three unique lines. Furthermore,

it is difficult to account for the occurrence of the metastable phase in this composition range. It means that there are two phases of close-packed hexagonal structure and identical axial ratios coexistent in the same deposit. If the interpretation of the nature of the β'-phase is correct, they may be thought of as two disconnected "sections" of a supposedly continuous phase. They differ only in the size of the unit cell, by which size one of them (ϵ) is identified as a stable phase at ordinary temperatures and the other (β') as metastable. Needless to say, this relation is not apt to exist.

General Discussion.—The unexpected complexity of the results obtained makes it difficult to draw a complete comparison between the electrodeposited and thermal alloys. The data bring out several interesting points, however, some of which may have a practical bearing.

The heterogeneous nature of the deposits is noteworthy. A consideration of Fig. 1 shows that the predominant phase in any alloy is the one predicted from the thermal equilibrium diagram. The minor phases are present in considerable amounts, however, and their presence cannot be predicted from the equilibrium diagram. There is a general overlapping of phases evident, particularly for the γ- and β-phases. The former, stable in the range 55–67% cadmium, may be found in electrodeposited alloys in the composition range 46–83% cadmium. The latter, stable in a narrow range at 50% cadmium, may be electrodeposited in alloys containing 46–78% cadmium. The η- and ϵ-phases and the α-phase seem to remain within their expected bounds.

Fink and Gerapostolou[8] have studied silver–cadmium deposits microscopically and have reported that pure silver is deposited first. It should be noted that the results of the x-ray diffraction analysis do not contradict this. For most of the deposits analyzed, the positions of the lines of the diffraction pattern for pure silver (if $a_0 = 4.068$ is used for calculating d_{hkl}) are already occupied by lines belonging to the patterns of other phases known to be present. Small amounts of silver, therefore, may or may not be present in the deposits. If an appreciable amount were present, the diffraction lines for the smaller spacings should be found.

It is not difficult to offer a reasonable explanation for the heterogeneous nature of the deposits. The composition of the plate deposited at any instant depends upon the relative concentration of silver and cadmium ions in the solution, particularly in the stationary film of electrolyte around the cathode. Generally this ratio will be such as to cause the deposition of the phase to be expected from the chemical analysis of the plate. Occasionally the ratio of silver to cadmium ions in the stationary film will

[8] Fink and Gerapostolou, *Metal Ind. (New York)*, **28**, 519, 562 (1930). The results of these authors do not bring out the complexity of the deposits. They distinguish only two phases—pure silver and a phase which appears brown and is a cadmium-rich alloy.

vary, due to momentary convection currents and other local conditions, and for short periods, then, the composition of the deposit will vary from the average composition, and the phase deposited will vary accordingly. The composition of some of the plates is such that, judging from the thermal equilibrium diagram, a mixture of two phases is to be expected even under uniform conditions of deposition.

A homogeneous deposit may have advantages which would make it preferable to a heterogeneous deposit for practical purposes. Certainly vigorous stirring during deposition should produce a more homogeneous deposit if the above explanation of the heterogeneity is correct. The effects of stirring, current density and temperature on the nature of the deposit are being investigated at the present time.

Summary

The crystal structures of electrodeposited silver–cadmium alloys ranging in composition from 96.0% cadmium to 31.0% cadmium have been obtained from x-ray diffraction data. All known factors, other than the composition of the plate, which might affect the structure of the alloys have been held constant.

The results are summarized in Table III and Fig. 1.

The most significant points brought out by the study are:

1. Every deposit consists of solid solutions or compounds. In no case is the deposit merely a mixture of cadmium and silver.

2. The phase stable in a given range of composition of the thermal alloys is the predominant phase in an electrodeposited alloy in that same composition range. Therefore the predominant phase in the electrodeposit may be predicted from its chemical composition.

3. In general the deposits are heterogeneous, containing appreciable amounts of phases which do not exist in an annealed alloy of the composition in question. The complete composition of the electrodeposit, therefore, cannot be predicted from its chemical composition.

4. There is little evidence indicating the formation of a metastable (β'-phase) deposit under the conditions of the experiment.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

MAGNETIC SUSCEPTIBILITY OF $Sm_2(SO_4)_3 \cdot 8H_2O$

BY F. H. SPEDDING*

RECEIVED NOVEMBER 30, 1931 PUBLISHED JULY 6, 1932

Hund[1] calculated values for the magnetic susceptibility of the rare earth ions, employing basic levels he had predicted from rules of spectra. His results, except for Sm^{+++} and Eu^{+++},[2] were in excellent agreement with the values which had been obtained experimentally with solids and solutions.

Freed[3] has shown very conclusively in his magnetic researches that the discrepancy in the case of Sm^{+++} is due to the presence of electronic isomers. That is, at very low temperatures the electronic configuration of most of the samarium ions is that predicted by Hund ($4f^5$, $^6H_{5/2}$). At higher temperatures, however, Freed showed that many of the atoms due to the Boltzmann distribution are in excited states, the energy values of which are but slightly greater than that of the $^6H_{5/2}$ term.

A confirmation of the existence of these isomers was found by Freed and Spedding[4] from the absorption spectrum of $SmCl_3 \cdot 6H_2O$ crystals. They found that as the temperature of the crystal was lowered certain lines tended to become more intense while others, usually a few hundred inverse centimeters to the red, faded out and finally disappeared.

At the time these researches were performed Freed was unable to determine the electronic configuration of the excited states as all the usual systems of coupling gave susceptibilities which could not be brought into accord with his data.

Since then from researches on the Gd^{+++} ion it has been shown[5] that a new type of magnetic coupling is probably effective in the case of the rare earths. In a letter to *Physical Review*,[6] experimental evidence was presented which showed that when a rare earth ion is excited, a 4f electron jumps through the 5s, 5p completed shells to a 5d, 5f or 5g orbit. Due to its electrical nature this orbit is strongly coupled to the electrical fields of the crystal and cannot orient in the magnetic fields obtainable in the laboratory.

It will, however, have a magnetic moment which will couple with the resultant moment of the remaining 4f electrons and the energy of this

* National Research Fellow.

[1] F. Hund, *Z. Physik*, **33**, 349 (1925).

[2] J. H. Van Vleck, *Phys. Rev.*, **31**, 587 (1928), has explained the discrepancy in the case of Eu^{+++}.

[3] Freed, THIS JOURNAL, **52**, 2702 (1930).

[4] Freed and Spedding, *Nature*, **123**, 525 (1929).

[5] F. H. Spedding, *Phys. Rev.*, **37**, 771 (1931).

[6] F. H. Spedding, *ibid.*, **38**, 2080 (1931).

coupling will presumably be so great that ordinary magnetic fields will not disrupt it. Therefore the 4f electrons will not contribute anything as a first approximation to the magnetic susceptibility of the ions. The spin of the external electron, however, will be loosely coupled, as its resonance effect with the other spins will be negligible due to the shielding action of the 5s, 5p shells and it will orient rather freely in ordinary magnetic fields. Thus all the excited levels will have a susceptibility corresponding to the spin of one electron.

While in gaseous Sm^{+++} ions one would expect the $(({}^5J_4\cdot d)_6)_{11/2}$ term to be the one of lowest energy, in solids, due to the effect of the surrounding ions in a crystal the $(({}^5J_4\cdot g)_8)_{15/2}$ or $(({}^5J_4\cdot f)_7)_{13/2}$ might be the lowest due to the greater symmetry of the f and g orbits. In any case the energy difference between them will not be great as they resemble somewhat the single electron in the alkali spectra.

If one assumes the basic level of Sm^{+++} ion in $Sm_2(SO_4)_3\cdot 8H_2O$ to be a ${}^6H_{5/2}$ which is free to orient in a magnetic field (Hund's assumption) and that the first excited level is a $(({}^5J_4.g)_8)_{15/2}$ in which the g orbit is bound, then the Curie constants per mole using the customary formula

$$C = \frac{N}{3k} j(j+1) g^2\beta^2$$

where N is Avogadro number, k Boltzmann constant, and β the Bohr magneton $eh/4\pi m_0 c$ will be

$$C_0 = \frac{g^2 j(i+1)}{(2.838)^2} = \frac{\left(\frac{2}{7}\right)^2 \frac{5}{2} \times \frac{7}{2}}{(2.838)^2} = 0.08867$$

for the normal state and

$$C_1 = \frac{2^2\left(\frac{1}{2} \times \frac{3}{2}\right)}{(2.838)^2} = 0.3724$$

for the excited states. The susceptibility at any temperature can be calculated from the relation[7]

$$\frac{C_0 N_0}{T + \Delta_1} + \frac{C_1(1 - N_0)}{T + \Delta_2} = \chi$$

where T is the absolute temperature, N_0 the percentage of ions in the normal state, χ is the susceptibility per mole, and Δ is a blanket correction factor, covering such factors as the effect of restraints on the free orientation of the permanent moment due to the coupling of the spin with the orbit in the excited states, and of the orbits with the crystal fields in the normal term. It would also include any magnetic contributions which might arise from having the orbits warp in the excited state.

[7] The Van Vleck "forgotten term" can be neglected here as the levels are well separated and do not belong to the same multiplet. When N_0 becomes 100% this equation becomes the Curie Weiss Law $\chi = C/(T + \Delta)$.

Not much is known about this Δ; however, in the case of $Er_2(SO_4)_3 \cdot 8H_2O$[8] where the basic level has a term composed of spin and orbital moments somewhat similar to $Sm_2(SO_4)_3 \cdot 8H_2O$ it is small, amounting to 1.9°K.

In these calculations both Δ_1 and Δ_2 were assumed to be 2°K. N_0 is calculated in the ordinary way[9]

$$\frac{1 - N_0}{N_0} = \frac{S_1 e^{-\frac{h\Delta\nu}{kT}}}{S_0(1)}$$

where S_1 and S_0 are the statistical weights of the levels and $\Delta\nu$ is the separation in inverse centimeters between them. Using one of Freed's experimentally determined points, $\Delta\nu$ was calculated. It is 195 cm.$^{-1}$. Then, using this value, other points on the curve were calculated. They are given in Table I and are in good agreement up to 150°K., after which they deviate. This deviation, however, is to be expected as other terms become effective at higher temperatures; the $(^5J_4 \cdot f_7)_{15/2\ 13/2}$ $((^5J_4 \cdot d)_6)_{13/2\ 11/2}$ are not much higher and also terms of the type $((^5J_4 \cdot g)_7)_{15/2\ 13/2}$ $((^5J_4 \cdot g)_6)_{13/2\ 11/2}$ would occur within a few hundred cm.$^{-1}$ of the $((^5J_4 \cdot g)_8)_{17/2}$ term.[10] From the equations it can be seen that χ is very sensitive to the value of C_1. The statistical weight of the excited state, since it enters into the calculation of N_0 only and not C, can be varied somewhat if $\Delta\nu$ and the Δ's are varied also as χ is not very sensitive to them when they are varied as a group. However, for states other than $(^5J_4 \cdot g)$ and $(^5J_4 \cdot f)$ the Δ's become so large as to seem improbable. Table II gives the calculated values for a $((^5J_4 \cdot f)_7)_{13/2\ 15/2}$ excited level. $\Delta\nu$ comes out 165 cm.$^{-1}$ and Δ has to be 7°K.

[8] De Haas, Wiersma and Capel, Leiden Communication 201b.

[9] The statistical weight of the lower level will be equal to $2j + 1$ or 6 as j is equal to 5/2. The statistical weight of the excited level depends on the fact that the g orbit is bound to the crystal field. This orbit can take $(2j + 1)$ orientations to this field or 9 since j is 4, and as the spin can be either with or against the orbit the total value is 2×9 or 18.

The contribution of the frozen 4f electrons enters into the weight in giving rise to terms of different energy such as $(^5J_4g)_8$ and $(^5J_4g)_7$, where, due to the bound orbit, the multiplicity is again 18.

$\Delta\nu$ is, of course, the mean distance between the weighted center of the multiplets as both upper and lower levels are non-degenerate due to the electric field of the crystals. (Some of these levels may become degenerate in crystals of high symmetry.) While the splitting in the lower level is negligible, it may be rather large in the excited state, amounting to 70 cm.$^{-1}$ or 80 cm.$^{-1}$ (as in the case of $GdCl_3 \cdot 6H_2O$). However, the weighted mean (according to the Boltzmann factor) is not very sensitive to temperature in the case calculated here.

[10] In the case of Gd^{+++} where the basic level is known to be single $(^8S_{7/2})$ there are over sixty lines occurring in the space of 700 cm.$^{-1}$. These excited terms are probably of the type

$$((^7F_1g)_5)_{9/2},\ ((^7F_1g)_4)_{7/2\ 9/2},\ ((^7F_1d)_3)_{5/2\ 7/2},\ \text{etc.}$$

The multiplet of lowest energy is well separated from the rest and they become closer together toward higher frequencies, just as would be expected.

TABLE I

MAGNETIC SUSCEPTIBILITY OF $Sm_2(SO_4)_3 \cdot 8H_2O$

Basic Level $^6H_{5/2}$, Curie Constant = C_0 = 0.08867. First excited level $((^5J_4 \cdot g)_{15/2})_{17/2}$, Curie Constant C = 0.3724. $\Delta\nu$ = 195 cm.$^{-1}$. Δ = 2° Å.

T, Absolute	N_0	N_1	N_0C_0	N_1C_1	Calcd. χ	Experimental χ
73.8	0.9359	0.0641	830	239	$\times 10^6$	$\times 10^6$
					1410	1402
80	.9159	.0841	813	313	1373	1375
90	.8808	.1192	781	444	1332	1338
100	.8443	.1557	749	580	1303	1308
120	.7716	.2284	684	851	1260	1254
140	.7096	.2904	629	1081	1205	1206
160	.6558	.3442	581	1282	1150	1171
180	.6107	.3893	542	1450	1094	1140
200	.5734	.4266	508	1589	1038	1119
250	.5042	.4958	447	1846	910	1065
300	.4578	.5422	406	2019	803	1035

TABLE II

MAGNETIC SUSCEPTIBILITY OF $Sm_2(SO_4)_3 \cdot 8H_2O$

Excited Level $((^5J_4 \cdot f)_7)_{13/2}$ $_{15/2}$. Δ = 7°. $\Delta\nu$ = 165 cm.$^{-1}$

T, Absolute	N_0	N_1	N_0C_0	N_1C_1	Calcd. $\chi \times 10^6$	Obs. $\chi \times 10^6$
73.8	0.9130	0.0870	810	324	1403	1402
80	.8912	.1088	790	405	1374	1375
90	.8551	.1449	758	540	1337	1338
100	.8196	.1804	727	672	1307	1308
120	.7519	.2481	667	924	1256	1254
140	.6982	.3018	619	1124	1185	1206
160	.6520	.3480	578	1296	1122	1171

From the above it would appear that the excited electronic isomers of $Sm_2(SO_4)_3 \cdot 8H_2O$ consist of $4f^65g$, $4f^65f$, $4f^65d$ configurations where the $4f^6$ electrons combine among themselves and the resultant couples firmly with the orbit of the excited electron, which itself is firmly coupled with the electric field of the crystal lattice. Thus only the spin of the external electron contributes to the magnetic susceptibility and all excited terms have a Curie constant of 0.3724. At present it is impossible to determine whether the excited electron in the first excited state is in a 5g or 5f orbit but it is hoped an answer will be found shortly from a study of the absorption spectra which is being carried out by Mr. Bear and myself.

Since the above paper was written considerable work has been done in this field.

Spedding and Bear, *Phys. Rev.*, **39**, 948 (1932), have investigated the absorption and reflection spectra of $SmCl_3 \cdot 6H_2O$ and have identified a group of levels occurring about 160 cm.$^{-1}$ above the basic level. Recently they have also identified another group of levels occurring between 250 cm.$^{-1}$ and 300 cm.$^{-1}$ from the basic level, just as predicted above, and will publish their results shortly in *Physical Review*. Preliminary photographs with $Sm_2(SO_4)_3 \cdot 8H_2O$ indicate that the same levels occur in approximately the same positions.

Ahlberg and Freed have measured the specific heats of $Sm_2(SO_4)_3 \cdot 8H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$, *ibid.*, **39**, 540 (1932), and have concluded that Sm^{+++} in $Sm_2(SO_4)_3 \cdot 8H_2O$

has "electronic isomers" which are separated from the basic level by about 160 cm.$^{-1}$ and which have approximately twice the statistical weight of the basic level. These values are in excellent agreement with those calculated in Table II above.

Amelia Frank, *ibid.*, **39**, 119 (1932), in extending the work of J. H. Van Vleck and A. Frank, has attempted an alternative explanation. In view of the experimental facts, her calculations cannot be correct as stated, as her first excited level occurs around 900 cm.$^{-1}$. However, the $^6H_{7/2}$ term would be expected to occur at a slightly greater value than that and at higher temperatures an effect such as they predict probably exists.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 318, AND FROM THE CHEMICAL LABORATORY AT THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE KINETICS OF THE REACTION BETWEEN POTASSIUM PERMANGANATE AND OXALIC ACID. I

BY HERBERT F. LAUNER

RECEIVED DECEMBER 21, 1931 PUBLISHED JULY 6, 1932

Introduction

The over-all reaction between permanganate and oxalic acid is expressed by the equation

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{++} + 10CO_2 + 8H_2O \qquad (1)$$

The rate of this reaction has been studied by several investigators[1] all of whom used an iodimetric method for the analysis of the reaction mixtures.

In this paper are presented the results of a new investigation of the reaction between permanganate ion and oxalate ion.

The author wishes to express here his appreciation of the aid and criticisms of Prof. Don M. Yost and Dr. J. B. Ramsey.

A large number of experiments were made on this reaction by an improved method which show that the mechanism previously suggested by Skrabal is not consistent with all of the experimentally found facts. Because of the rather complicated nature of the reaction the outstanding experimental results and theoretical conclusions will, for greater clearness, be stated briefly at this point.

When a solution of permanganate ion is added to one of manganous ion in which acid and oxalate ion are also present, a cherry-red solution of a complex ion formed from manganic ion and oxalate ion results, whereas in the absence of oxalate ion or other anion capable of forming a complex, a precipitate of manganese dioxide is obtained. It will be shown that the formula of the manganic complex ion is $Mn(C_2O_4)_2^-$.

The rate of the reaction when manganous ion was present initially in

[1] Harcourt and Esson, *Phil. Trans.*, 201 (1866); Schilow, *Ber.*, **36**, 2735 (1903); Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904).

excess and when the solution was in contact with a constant gas space was found to be represented by the following differential equation

$$\frac{dp_{CO_2}}{dt} = \frac{k_1(Mn(C_2O_4)_2^-)}{(C_2O_4^=)} \quad (2)$$

The following series of reactions provides a mechanism that is in accord with equation (2).

$MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O$	(rapid)	(3)
$Mn^{+++} + 2C_2O_4^= = Mn(C_2O_4)_2^-$	(rapid, reversible)	(4)
$Mn^{+++} + C_2O_4^= = Mn^{++} + CO_2 + CO_2^-$	(measurable)	(5)
$Mn^{+++} + CO_2^- = Mn^{++} + CO_2$	(rapid)	(6)

It will be noted that the existence of an unknown ion CO_2^- is postulated in equation 5—a matter which is further considered below. Reaction 3 is to be regarded in the present connection only as the source of tripositive manganese, the concentration of whose ion (Mn^{+++}) is determined by the equilibrium conditions of reaction 4. This reaction also involves the concentration of oxalate ion, which is itself dependent upon the acidity of the solution. The rate of the reaction is then determined by reaction 5, whose rate should be expressed by the equation

$$\frac{dp_{CO_2}}{dt} = k_2(Mn^{+++})(C_2O_4^=) \quad (7)$$

By substituting for (Mn^{+++}) in equation 7 the expression $(1/K_4)(MnC_2O_4^-)/(C_2O_4^=)^2$ given by the mass action law, there results equation 2, which was found to express the experimental results.

This mechanism is in sharp contrast with that of Skrabal, which required that the measurable step be the dissociation of a manganic–oxalate complex, and that the reaction in which manganic ion is reduced be rapid and of third order.

Method of Experimentation

An apparatus for measuring the pressures of carbon dioxide produced was constructed and is shown diagrammatically in Fig. 1. In the reaction vessel was placed 90 cc. of solution, containing all but one of the reactants. Since the apparatus is rigid above the thermostat, a jar, kept overflowing with water from the thermostat, may be raised so that C is surrounded by water of the desired temperature. The stirrer A is so constructed that it not only churns the liquid but also forces the vapor phase through the liquid. The stirrer is connected to the system by means of the mercury seal K which is so designed that the maximum increase in pressure, accompanied by a difference in mercury levels in the seal, will cause a negligibly small increase (less than 1%) in the volume of the vapor phase.

From the buret 10 cc. of the last reactant was then introduced, the stopcock F_1 was closed, and readings were taken on the water manometer at suitable intervals. The reservoir D contains the water that must be forced up the manometer tube on the scale G in order that the hydrostatic pressure balance the gas pressure in C, and that the meniscus I return to its initial position.

The pressures p_{CO_2} of carbon dioxide as read on the manometer are proportional to the number of moles of carbon dioxide evolved in the reaction, inasmuch as carbon di-

oxide obeys Henry's law at pressures of one-tenth atmosphere and inasmuch as the volume and temperature are essentially constant. The total pressure in the system was always in the neighborhood of one atmosphere.

A series of blank experiments in which the rate of stirring was varied over wide limits above a certain high value, all gave the same curve, showing that equilibrium between the gas and liquid phases was established with sufficient rapidity.

All experiments were carried out at 25.14 ± 0.02°. Although most of the specific reaction rates show some trend, yet a comparison of the slopes at corresponding points on two curves (representing systems which differ only in the concentration of one component) allows conclusions to be drawn as to the effect of that component on the reaction rate, and as to the order of the reaction with respect to that component. The best obtainable materials were used throughout.

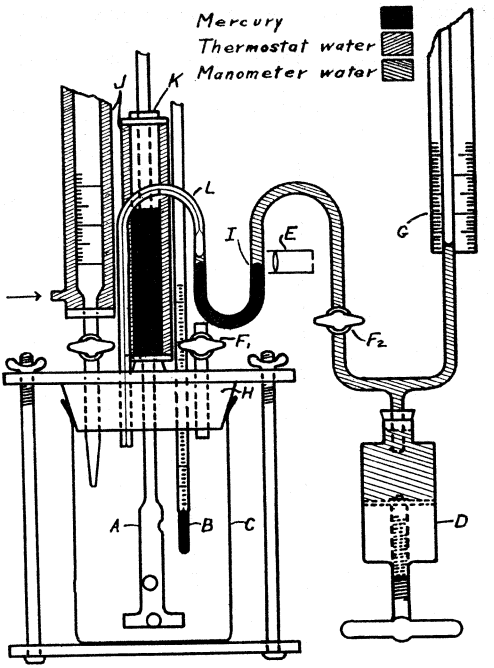


Fig. 1.—Gasometric apparatus: *A*, special centrifuging stirrer; *B*, thermometer; *C*, reaction vessel (a 200 cc. spoutless beaker); *D*, manometer-water reservoir (an "Alemite" grease gun); *E*, small thermometer telescope to observe meniscus I; F_1 and F_2, stopcocks; *G*, meter stick; *H*, rubber stopper, size 12; *I*, meniscus of mercury; *J*, water jackets through which is circulated (by a small pump) water, from thermostat; *K*, mercury seal device; *L*, capillary tubing.

The Effect of Manganous Ion on the Reaction Rate.—With the exception of one series all rate data are grouped at the end of this article.

The typical "induction" curve, curve (1), Fig. 2 (corresponding to experiment (1)), was obtained when no manganous ion was initially added. As indicated, point P is coincident with an abrupt color change in the solution. The abrupt simultaneous changes of rate and color make it seem reasonable that curve (1) from O to P represents at least three changes in the oxidation states of manganese, one from permanganate to some intermediate state, another from the intermediate state to the manganic state, and the third from the manganic state to the manganous state. From point P to the end, however, the curve seems to represent only the change from the manganic to the manganous state, the steadily increasing manganous ion concentration having served to eliminate all stages of manganese higher than the tripositive one.

The Existence of the Manganic Oxalate and Fluoride Complexes.—In

experiment (2), represented by curve (2), Fig. 2, the manganous ion initially present served to reduce the permanganate as rapidly as the latter could be added, with the formation of a cherry-red solution.

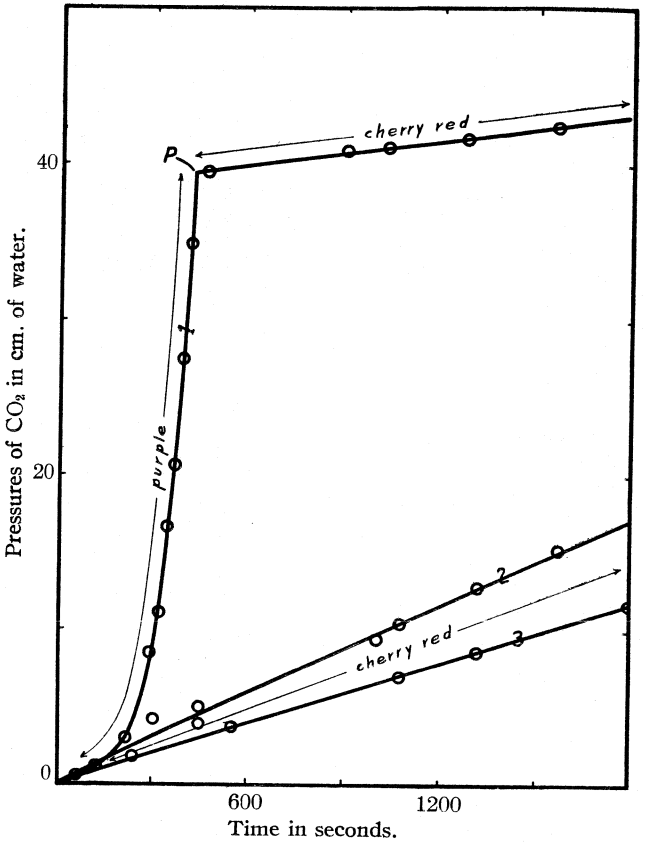


Fig. 2.—The effect of manganous ion and acid.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	H_2SO_4	$K_2C_2O_4$	$MnSO_4$
1	1	98.4	246	0
2	1	98.4	246	13
3	1	72.2	246	13

To prove that the cherry-red color is due to tripositive manganese the following experiment was performed. Two equal portions of permanganate solution were treated with an excess of manganous ion in slightly acid solution. The manganese dioxide precipitates were each filtered and washed free from manganous ion. One portion was placed in an acidified potassium iodide solution and the liberated iodine titrated with thiosulfate, of which 20.10 cc. was required. The other portion was placed in a solution

of sulfuric acid and potassium oxalate like that of experiment (1). The manganese dioxide dissolved rapidly and gave a cherry-red solution, indistinguishable in color from those previously observed. Potassium iodide was immediately added and the iodine titrated, using this time 9.95 cc. of thiosulfate. The tetrapositive manganese evidently lost one-half of its oxidizing power and was converted therefore into the manganic state, the latter being responsible for the color observed above. The reaction that took place was evidently

$$2MnO_2 + (2n + 1)C_2O_4^{=} = 2Mn(C_2O_4)_n^{-} + 2CO_2 \qquad (8)$$

Next, freshly precipitated manganese dioxide was introduced into an acidified solution of potassium fluoride. No manganese dioxide dissolved until manganous ion was added, whereupon the rapid reaction

$$4H^+ + MnO_2 + Mn^{++} = 2Mn^{+++} + 2H_2O \qquad (9)$$

doubtless took place with the subsequent formation of a manganic fluoride complex.

The Effect of Acid, Oxalate Ion and Manganic Ion on the Reaction Rate.—A comparison of curves (2) and (3), Fig. 2, shows the effect of acid on the rate. It is to be noted, however, that the concentration of oxalate ion is inversely proportional to the concentration of hydrogen ion, since oxalic acid is weak. The following experiments show that acid is without influence on the rate if the concentration of oxalate ion is fixed. A buffer, consisting of a mixture of acetic acid and ammonium acetate, served to maintain constant the concentration of the oxalate ion. The concentration of hydrogen ion could be varied four-fold while that of the oxalate ion remained essentially constant. Independent experiments showed that the acetic acid is stable in the presence of manganic salts.

TABLE I

THE EFFECT OF ACID ON THE REACTION RATE

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	CH_3COOH	$K_2C_2O_4$	CH_3COONH_4	$MnSO_4$
4	1	131	25	985	13
5	1	262	25	985	13
6	1	524	25	985	13

4		5		6	
Time in min.:sec.	Pressures, cm. H_2O	Time in min.:sec.	Pressures, cm. H_2O	Time in min.:sec.	Pressures, cm. H_2O
2:00	5.1	2:00	5.1	2:00	5.3
6:10	14.2	6:10	14.0	6:10	14.5
9:30	19.7	9:30	19.8	9:40	20.6
19:20	31.2	19:20	32.1	19:20	32.3
24:00	35.1	24:00	36.2	24:00	36.5
28:30	38.1	28:30	38.8	28:30	39.2

The rates vary only 1–2% while the acidity varies 200%, the concentration of oxalate ion remaining essentially constant. The results show

that the effect of acid upon the rate is due solely to its effect on the concentration of oxalate ion.

A series of experiments was made in which the acidity and ionic strength were maintained constant while the concentration of oxalate ion was varied. In preliminary experiments the quinhydrone electrode was used to determine the relative proportions of sulfuric acid and potassium oxalate

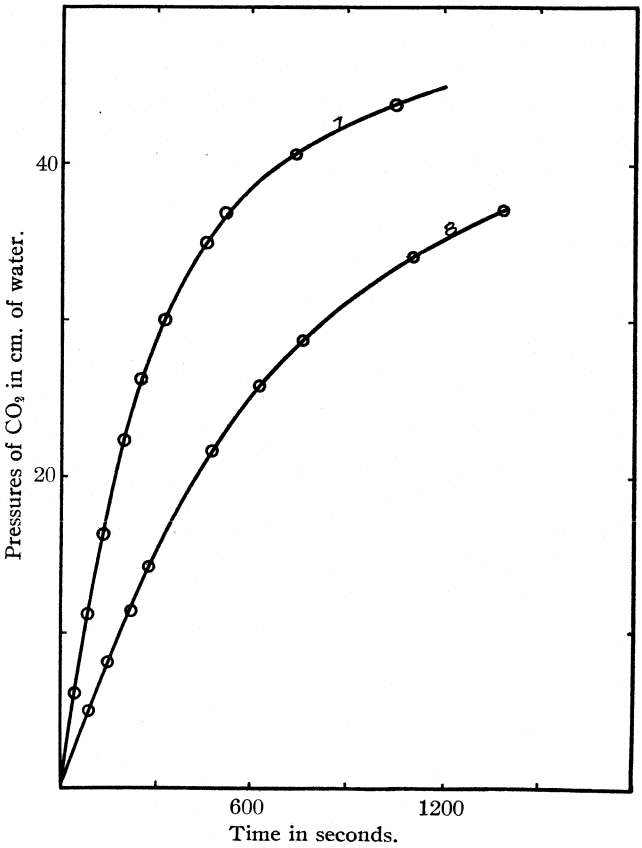


Fig. 3.—The effect of oxalate ion.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	$K_2C_2O_4$	H_2SO_4	K_2SO_4	$MnSO_4$	Activity of H^+
7	1	50	142	130	13	0.0276
8	1	125	164	0	13	.0276

necessary to keep the activity of the hydrogen ion, and hence its concentration, constant. The potassium sulfate was used to adjust the ionic strength of the solutions. In Fig. 3 the slopes of curve (7) are 2.5 times the slopes of curve (8) at corresponding points, while the concentration of oxalate ion in (8) was 2.5 times that in (7).

Next, a mixture of potassium sulfate, bisulfate and acid oxalate was used to keep the acidity fixed but to permit the oxalate-ion concentration to vary. In Fig. 4 the slopes of curve (9) are twice those of curve (10) and four times those of curve (11) at corresponding points, the concentration

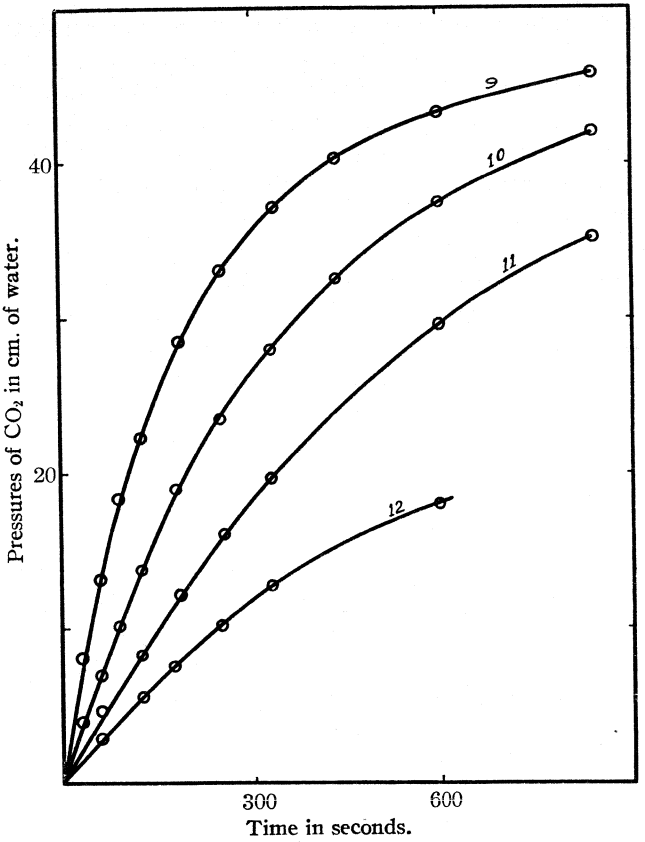


Fig. 4.—The effect of oxalate ion.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	KHC_2O_4	$KHSO_4$	K_2SO_4	$MnSO_4$
9	1	29	271	200	13
10	1	58	271	200	13
11	1	116	271	200	13
12	0.5	58	271	200	13

of oxalate ion in (10) and (11) being twice and four times, respectively, that in (9). From these results it follows that the rate is inversely proportional to the oxalate-ion concentration.

From the results of previous investigators,[1] and also from the fact that in Fig. 4 the slopes of curve (10) are twice those of curve (12), the concen-

tration of oxidizing agent being in the ratio of two to one, it is evident that the reaction is first order with respect to the oxidizing agent. The concentration of the oxidizing agent is essentially equal to the concentration of the complex manganic oxalate anion since this complex dissociates but little, as will be shown below.

It is evident that the effect of oxalate ion on the rate of reaction (5) (see Introduction) was not directly observable because of its effect on the concentration of manganic ion as shown by equation (4). Experiments were next made in which fluoride was added to suppress the formation of the manganic oxalate complex through the formation of a fluoride complex. This served to make the concentration of manganic ion independent of the concentration of oxalate ion.

Rather crude experiments, the details of which will be given later, show that the manganic fluoride complex is much more dissociated than the manganic oxalate complex. The equilibrium between the two complexes may be represented by the following chemical equation. (It will be shown later that the formulas given for the complexes are probably correct.)

$$Mn(C_2O_4)_2^- + 4F^- = MnF_4^- + 2C_2O_4^- \qquad (10)$$

The mass action expression for (10) is

$$\frac{(MnF_4^-)(C_2O_4^=)^2}{(Mn(C_2O_4)_2)(F^-)^4} = \frac{K}{K_4} = K_{10} \qquad (11)$$

In equation (11), K_{10}, which is the ratio of the dissociation constants of the two complexes, has a value of approximately 0.05, and the ratio $(C_2O_4^=):(F^-)$ must be 1:7 as a maximum value, if 99% of the manganic ion is to be in the fluoride complex. This condition was attained by placing the reducing agent in deficiency and the oxidizing agent in such excess that changes in the concentration of the latter during the first third of each experiment were negligible.

In Fig. 5 the slopes of curve (17) are twice those of curve (19), and the slopes of curve (18) are twice those of curve (20). Also, the slopes of curves (18) and (19) are equal (at corresponding points). Since, as may be seen from the data given under Fig. 5, the various concentrations are, at corresponding points, in the same ratio as the slopes just compared, it follows that the rate is directly proportional to the concentrations of manganic and oxalate ion. This indicates, therefore, that the slow step is the oxidation of oxalate ion by manganic ion (reaction 5) and not the dissociation of the manganic oxalate complex as assumed by Skrabal.

The Manganic Oxalate and Fluoride Complexes.—Aside from reaction rate data it is desirable to prove that the formula of the manganic oxalate complex is $Mn(C_2O_4)_2^-$.

The following experiments were based on the fact that if the concentration of manganic ion exceeds a certain value manganese dioxide will

precipitate. In each experiment was determined the concentration of oxalate or fluoride ion necessary to prevent the formation of manganese dioxide from a given amount of permanganate, manganous ion and sulfuric acid.

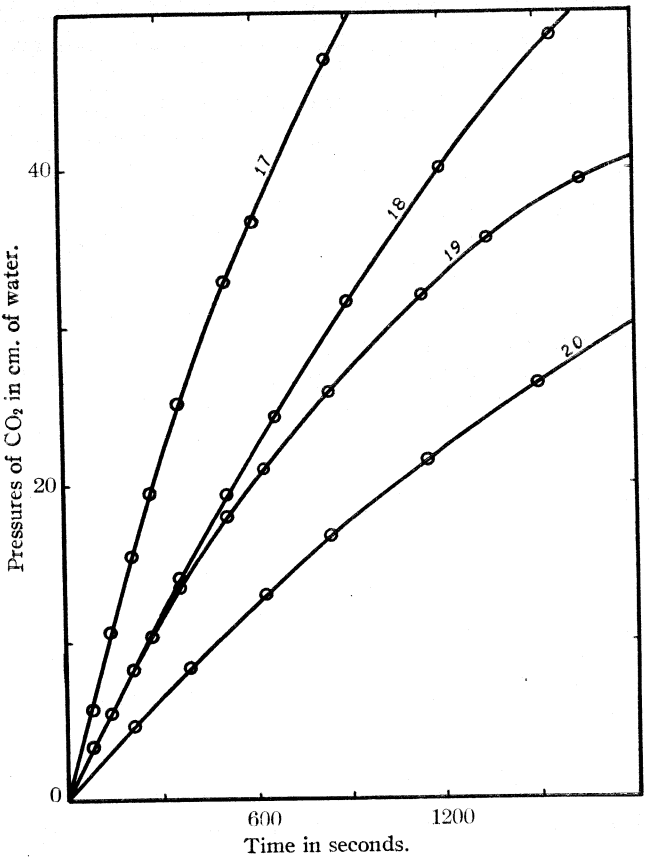


Fig. 5.—The effect of oxalate ion when tripositive manganese is present principally as a complex fluoride.

	Formula weights in 647 liters of solution					
Experiment	KHC_2O_4	$KMnO_4$	$MnSO_4$	KF	$KHSO_4$	$(NH_4)_2SO_4$
17	2	2.36 (6-fold excess)	26	155	201	65
18	2	1.18 (3-fold excess)	13	155	201	65
19	1	2.36 (12-fold excess)	26	155	201	65
20	1	1.18 (6-fold excess)	13	155	201	65

Equal portions of permanganate were added to solutions consisting of an excess of acid and of manganous ion, and of varying amounts of potassium oxalate such that the ratio moles of $K_2C_2O_4$: moles of tripositive manganese was 1.00, 1.25, 1.5, 1.75, 1.875 and 2.00. Only in the last case was a clear

solution obtained, thus showing that two oxalate ions combine with one manganic ion to form the complex.

With this information the following experiment was carried out. Ten (10.00) cc. of 0.00762 *M* permanganate (equivalent to 39.20 cc. of thiosulfate) was added to 6.80 cc. of a solution consisting of manganous ion in excess and 0.0007415 mole of potassium acid oxalate. One drop more caused a precipitate of manganese dioxide. This solution was immediately treated with iodide ion and acid. The volume of thiosulfate now necessary was 36.80 cc. From this the following concentrations were calculated

	KHC_2O_4 remaining	0.04340 *M*
	MnIII remaining	0.02125 *M*
Hence	$Mn(C_2O_4)_2^-$ remaining	0.02125 *M*
and	$C_2O_4^=$ remaining (maximum)	0.00090 *M*

By analogy to the manganic oxalate complex the formula MnF_4^- was adopted as being the probable one. Next, 0.90 cc. of 0.00762 *M* permanganate was added to 20 cc. of a solution consisting of 0.000824 mole of potassium fluoride, 0.0005 mole of sulfuric acid and 0.00101 mole of manganous sulfate. A clear solution was obtained which gave a precipitate of manganese dioxide upon the addition of one more drop of permanganate. The concentrations of fluoride ion and of the manganic fluoride complex were calculated to be 0.03285 *M* and 0.001638 *M*, respectively. Since now the concentrations of free manganic ion in both this experiment and the oxalate experiment were such that a precipitation of manganese dioxide was barely averted, it may be assumed that the manganic ion concentration was the same in both experiments. The concentrations of the two complexes and the fluoride and oxalate ion may, accordingly, be substituted in equation (11) and yield for K_{10} the value 0.05.

These experiments indicate that the formula of the manganic oxalate complex is $Mn(C_2O_4)_2^-$, and give the minimum value for the ratio (F^-): $(C_2O^=)$ necessary to have tripositive manganese present mainly as the fluoride complex.

In the following experiments, (21) and (22), Fig. 6, the oxalate ion concentration remained unchanged, but the acid oxalate ion concentration varied five-fold. The slight difference in rate indicates that it is the oxalate ion, and not the acid oxalate ion, which forms the complex and which reacts as in equation (5).

Curve (21′), Fig. 6, would represent approximately the rate in experiment (21) if the acid oxalate ion were the principal complex-former.

The Effect of Ionic Strength on the Rate.—In the foregoing experiments precautions were taken to minimize changes in rate due to changes in the ionic strength. A comparison between the curves for experiments (22) and (23), Fig. 6, which differ only in ionic strength, shows that

there is a large positive salt effect on the rate. The change in rate was approximately 500% while the change in the solubility of carbon dioxide was

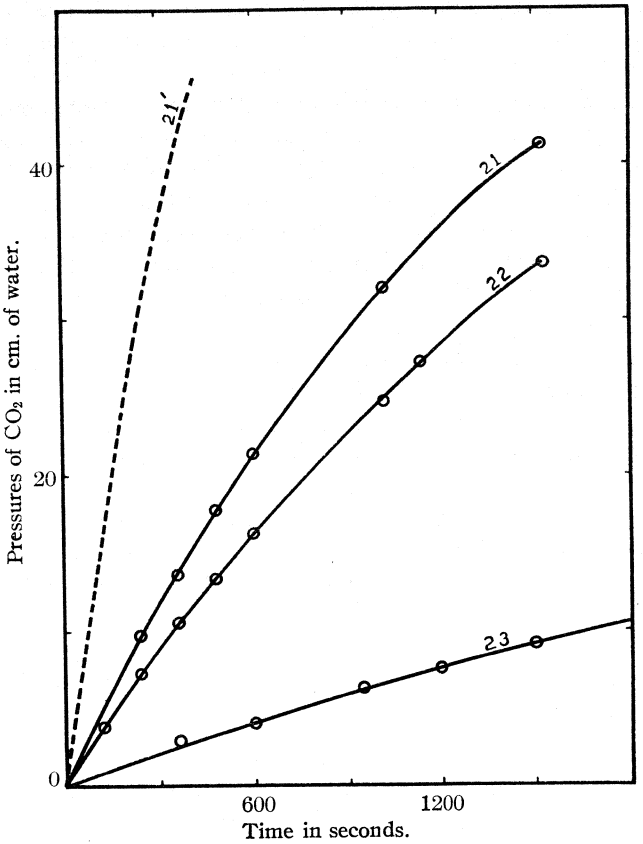


Fig. 6.—The effect of binoxalate ion and the ionic strength on the rate.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	$K_2C_2O_4$	KHC_2O_4	$(NH_4)_2SO_4$	$MnSO_4$	Ionic strength
21	1	49	28	1310	13	3.26
22	1	49	140	1310	13	3.26
23	1	49	140	0	13	0.26

small, 15%, compared to this. When modified by Brönsted's rate hypothesis the experimentally determined rate equation (2) becomes

$$\frac{dp_{CO_2}}{dt} = \frac{k(Mn(C_2O_4)_2^-)}{(C_2O_4^=)} \cdot \frac{f_1}{f_2 f_3}$$

where f_1, f_2 and f_3 are the activity coefficients of the manganic oxalate complex, the oxalate ion and the unipositive critical complex ion, respectively. This expression, after cancellation of the activity coefficients of the

two singly charged ions, evidently requires that the rate increase rapidly with the ionic strength and this was found experimentally to be the case.

The experimental results presented above are all in accord with the mechanism already described. It is believed that the method of experimentation used has made possible a more precise determination of the mechanism than was possible in the previous studies of the reaction.

The Role of Peroxides in the Manganic Oxalate Reaction.—If the manganic oxalate reaction be allowed to run to completion in the presence of oxygen, the resulting solution will impart a yellow color to a solution of titanic sulfate. The existence of hydrogen peroxide during the permanganate titration has been observed and studied by Kolthoff.[2]

It is suggested here that the hydrogen peroxide arises from an equilibrium between water and a peroxide of carbon, and that this latter results from a combination of the O_2 molecule and the CO_2^- ion in an effort on the part of both particles to form an electron-pair bond from their unpaired electrons. Rate data show that in the first effective collision between a manganic ion and an oxalate ion, one electron is removed from the latter. This leaves only one electron between the two carbon atoms. Since one electron ordinarily does not constitute a stable chemical bond, the carbon atoms part, becoming CO_2 and CO_2^-, a particle with an unpaired electron. In a later paper on the effect of oxygen upon this reaction will be presented results in support of the above ideas.

The curves given were drawn using the data presented in Table II. The numbers assigned to the curves are the same as those of the corresponding experiments.

TABLE II

RESULTS OF THE RATE MEASUREMENTS

Experiment (1)		Experiment (2)		Experiment (3)		Experiment (7)	
Time in min.:sec.	Press. CO_2 in cm. H_2O	Time in min.:sec.	Press. CO_2 in cm. H_2O	Time in min.:sec.	Press. CO_2 in cm. H_2O	Time in min.:sec.	Press. CO_2 in cm. H_2O
1:00	0.5	3:45	2.9	4:00	1.8	0:45	6.1
2:00	1.2	5:05	4.2	7:30	3.9	1:25	11.2
3:40	3.0	7:30	5.0	18:00	7.0	2:25	18.0
4:50	8.5	16:45	9.4	22:00	8.6	3:20	22.3
5:20	11.1	18:00	10.4	30:00	11.7	4:15	26.2
5:40	15.1	22:00	12.7	45:00	17.1	5:30	30.0
6:05	20.6	26:15	15.2	55:00	20.3	7:40	34.9
6:30	27.4	30:00	17.1	∞	60.2	8:40	36.8
6:35	34.8	42:30	22.9			12:20	40.6
7:45	39.4	45:50	24.2			17:30	43.8
15:00	40.8	51:30	26.4			∞	48.0
17:10	41.0	56:10	28.4				
21:15	41.6	∞	60.2				
26:00	42.4						
∞	60.2						

[2] Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924).

TABLE II (*Concluded*)

(8) Time in min.:sec.	Press. CO_2* in cm. H_2O	(9) Time in min.:sec.	Press. CO_2 in cm. H_2O	(10) Time in min.:sec.	Press. CO_2 in cm. H_2O	(11) Time in min.:sec.	Press. CO_2 in cm. H_2O
0:40	2.6	0:30	8.1	0:30	4.0	0:30	2.6
1:30	5.0	1:00	13.2	1:00	7.0	1:00	4.7
2:30	8.1	1:30	18.4	1:30	10.2	1:30	6.2
3:45	11.4	2:05	22.3	2:05	13.8	2:05	8.3
4:40	14.2	3:05	28.5	3:00	19.0	3:05	12.2
8:00	21.6	4:10	33.1	4:10	23.5	4:15	16.1
10:30	25.8	5:35	37.2	5:30	28.0	5:30	19.7
12:45	28.7	7:15	40.3	7:15	32.6	10:00	29.6
18:25	34.1	10:50	43.3	10:00	37.5	14:00	35.2
23:05	37.1	14:00	45.8	14:00	42.0	∞	47.0
∞	48.0	∞	47.0	∞	47.0		

(12)		(17)		(18)		(19)	
0:30	1.5	1:20	5.8	3:30	8.3	1:20	3.4
1:00	2.9	2:20	10.7	6:00	14.1	2:20	5.5
1:30	4.2	3:30	15.5	8:30	19.4	3:30	8.3
2:05	5.6	4:30	19.5	11:05	24.3	4:30	10.4
3:00	7.6	6:00	25.1	15:00	31.6	6:00	13.5
4:10	10.2	8:30	32.9	20:00	40.1	8:30	18.0
5:30	12.8	10:00	36.7	26:00	46.5	10:30	21.0
10:00	18.0	14:00	47.0	30:00	53.7	14:00	25.9
∞	23.5	22:00	63.6	38:00	63.2	19:00	32.0
		∞	104.0	∞	104.0	22:30	35.6
						27:20	39.3
						∞	52.0

(20)		(21)		(22)		(23)	
1:20	1.9	4:00	9.7	1:00	2.1	6:00	2.9
2:30	3.6	6:00	13.6	2:00	3.8	10:00	4.0
3:30	4.7	8:00	17.7	4:00	7.2	16:00	6.2
4:30	5.8	10:00	21.3	6:00	10.5	20:00	7.5
6:30	8.4	17:00	32.0	8:00	13.3	25:00	9.1
10:30	13.0	19:00	34.5	10:00	16.2	30:00	10.9
14:00	16 7	25:30	41.2	17:00	24.7	∞	47.0
19:10	21.5	∞	55.0	19.00	27.2		
25:00	26.4			21:00	29.2		
31:00	31.0			25:30	33.6		
∞	52.0			∞	55.0		

Summary

An apparatus was designed for the measurement of rapid reactions in solutions involving even exceedingly small quantities of gaseous product (0.02 millimole) provided either that this gas follow Henry's law or that the deviations therefrom be known.

The reaction between tripositive manganese and oxalate ion has been studied and found, in agreement with the work of previous investigators, to be an important step in the reaction between permanganate and oxalic acid. The rate of this reaction was found to be expressible by the equation

$$\frac{dp_{CO_2}}{dt} = k_1 \frac{(Mn(C_2O_4)_2^-)}{(C_2O_4^=)}$$

when oxalate ion is in excess, and by the equation

$$\frac{dp_{CO_2}}{dt} = k_2(Mn^{+++})(C_2O_4^=)$$

when oxalate ion is in deficiency and fluoride ion is present to form a complex with manganic ion. This led to the adoption of the following mechanism.

$$Mn^{+++} + 2C_2O_4^- = Mn(C_2O_4)_2^- \quad \text{(rapid, reversible)}$$
$$Mn^{+++} + C_2O_4^- = Mn^{++} + CO_2 + CO_2^- \quad \text{(measurable)}$$
$$Mn^{+++} + CO_2^- = Mn^{++} + CO_2 \quad \text{(rapid)}$$

The formula of the manganic oxalate complex ion was found to be $Mn(C_2O_4)_2^-$.

The influence of the ionic strength on the rate was found to be in accord with that predicted using the Brönsted hypothesis.

An explanation was proposed for the formation of peroxides when the reaction takes place in the presence of oxygen.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY AND ENTROPY OF CARBON MONOXIDE. HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID. FREE ENERGY TO 5000°K. FROM SPECTROSCOPIC DATA

BY J. O. CLAYTON[1] AND W. F. GIAUQUE

RECEIVED DECEMBER 28, 1931 PUBLISHED JULY 6, 1932

Carbon monoxide gas is one of the simpler diatomic molecules. Spectroscopically the normal level is a $^1\Sigma$ state and it has no other electronic configurations that are appreciably occupied until temperatures far in excess of the 5000°K. limit of our calculations are reached. While nuclear spin should not produce any appreciable effect on the observed behavior of such a molecule, it is of interest to note that the predominant isotopes of both carbon and oxygen are without nuclear spin.

In view of the molecular simplicity it might be expected that the entropy obtained from the band spectrum would agree with that obtained from the ordinary application of the third law. However, this proves not to be the case and it becomes a matter of considerable practical as well as theoretical interest to determine the extent to which similar effects may exist in other molecules. In attempting to find a definite physical explanation for the discrepancy it is desirable to have an accurate quantitative measure of the amount.

It is also our purpose to consider the equilibrium C (graphite) + $^1/_2O_2$ =

[1] Shell Research Fellow, Academic year 1929–30.

CO, combining thermal data on graphite and the accurately known heat of reaction with spectroscopic data on oxygen and carbon monoxide.

Preparation of Carbon Monoxide.—The carbon monoxide was made by the well-known method of dropping formic acid into concentrated sulfuric acid. The chemically pure reagents were boiled to remove dissolved gases and were later subjected to a vacuum in the closed preparation system. The formic acid was cooled with ice during the latter procedure to prevent too rapid evaporation. The preparation system was evacuated by means of a mercury diffusion pump and found to be vacuum tight before the reagents were introduced. The first portion of the carbon monoxide to be prepared was discarded. The carbon monoxide was passed through a 50% potassium hydroxide solution and then over phosphorus pentoxide. It was then condensed in liquid air and distilled three times, the first and last portions of each distillation being discarded.

Heat Capacity Measurements and Data.—The measurements of heat capacity were carried out in gold calorimeter II described by Giauque and Wiebe.[2] The method was the same as that given by the above authors and by Giauque and Johnston.[3] The discussion of the various factors affecting accuracy and the estimation of the accuracy at various temperatures has been given in the latter paper and applies to the present work. It is believed that the entropy may be computed from the results with an accuracy of two-tenths of one per cent.

Three preparations of carbon monoxide were used in the measurements. These are referred to as I, II and III.

The temperature standard was the copper–constantan thermocouple "W" of Giauque, Buffington and Schulze.[4] Since the original comparison with the hydrogen gas thermometer it has frequently been checked against the vapor pressure of oxygen. This comparison was repeated in the course of the present experiments and it was found to agree within a few hundredths of a degree at several temperatures in the liquid oxygen range. This is within the limit of the accuracy claimed, namely, 0.05°.

The temperature intervals and warming rates were all measured by means of the gold resistance thermometer. In correcting for the heat effect due to vaporization into the small gas volume above the condensed gas, during a temperature rise, the density of the liquid was taken from the work of Baly and Donnan[5]

$$d_{(l)} = 1.1604 - 0.0045\,T$$

As the volume of the solid is not very important in the above correction, it could be estimated with sufficient accuracy by comparison with nitrogen.

[2] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).
[3] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).
[4] Giauque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927).
[5] Baly and Donnan, *J. Chem. Soc.*, **81**, 907 (1902).

The amount of material was measured by means of the five-liter volumetric apparatus described by Giauque and Johnston.[3] Between series II and III an accident to the measuring bulb necessitated replacement, which was done with the same precautions described for the previous apparatus. The amount of material was determined as follows:

$$\text{Number of moles} = V \times P \times \frac{D}{M} \times \frac{1}{1 + KT}[1 + \alpha(1 - P)]$$

Gas density at 0 °C.	D =	1.2504 g./l.[6,7]
Molecular weight	M =	28.000
Coefficient of thermal expansion (0–100 °C.)	K =	0.003669[8]
Coefficient of deviation from Boyle's law (per atmosphere)	α =	−0.0005[9]
Gravitational acceleration (at Berkeley)	=	979.973 cm./sec.[10]

The value 4.185 absolute joules equal to 1 calorie (15°) was used in converting the electrical units to calories. The relation 1.00042 absolute joules = 1 international joule was used in calculating the energy.

The heat capacity results are given in Table I.

TABLE I

HEAT CAPACITY OF CARBON MONOXIDE

Molecular weight 28.000

T, degrees absolute	ΔT	C_P, calories per degree per mole	Series
14.36	2.640	1.637	I
16.94	2.153	2.458	I
19.37	2.328	3.268	I
21.93	2.213	3.976	I
24.31	2.172	4.573	I
26.64	2.284	5.114	I
29.01	2.345	5.681	I
31.56	2.696	6.272	I
39.85	3.001	8.111	I
44.21	3.403	9.055	I
44.71	2.293	9.089	III
47.90	3.837	9.888	I
48.34	4.427	9.937	III
52.34	3.909	11.01	I
55.07	4.775	11.73	III
56.82	4.901	12.71	I
59.04	3.025	13.61	III
61.55	Transition		
63.47	2.209	12.02	II
64.55	3.570	12.16	III
66.02	2.569	12.30	I
68.09	Melting Point		

[6] Moissan, *Compt. rend.*, **102** (1886).

[7] Rayleigh, *Proc. Roy. Soc.* (London), **A62**, 204 (1897).

[8] Regnault, *Ann. chim.*, **5**, 52 (1842).

[9] Schlatter, Thesis, Geneva, 1923.

[10] Sternewarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Berlin, 1923.

TABLE I (*Concluded*)

T, degrees absolute	ΔT	C_P, calories per degree per mole	Series
70.02	2.227	14.42	I
72.17	3.804	14.43	II
75.47	2.623	14.48	II
75.80	4.577	14.39	I
78.78	3.890	14.41	II
79.06	4.566	14.48	I
80.61	4.829	14.50	I
83.39	3.877	14.40	I
84.66	2.716	14.45	I

Series I, 2.7594 moles. Series II, 2.8414 moles. Series III, 2.5830 moles.

The heat capacity of carbon monoxide has been measured by Eucken[11] and by Clusius.[12]

The results of Clusius agree quite well with the present investigation, the largest deviations being below 20°K. and near the boiling point. The average deviation is about 3%. However, the algebraic deviation is only about 0.1%, showing agreement as to total energy input over the region. The earlier work of Eucken does not agree as well.

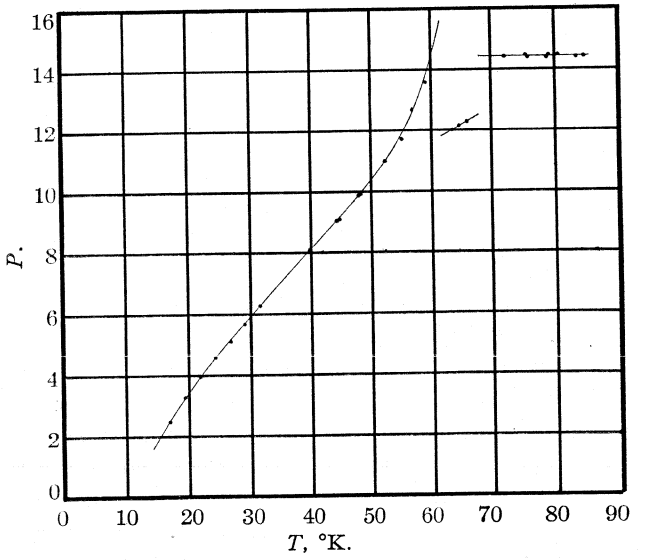


Fig. 1.—Capacity of carbon monoxide in calories per degree per mole.

The results given in Table I are shown graphically in Fig. 1.

Transition and Melting Point Temperatures.—The transition and melting point temperatures were investigated with various percentages trans-

[11] Eucken, *Ber.*, **18**, 4 (1916).

[12] Clusius, *Z. physik. Chem.*, [B] **3**, 41 (1929).

formed. The transition temperature was observed over a period of nineteen hours, the melting point for eighteen hours with preparation I and for sixteen hours with preparation II. The data are collected in Table II.

TABLE II

TRANSITION AND MELTING POINT TEMPERATURES OF CARBON MONOXIDE

Transition temperature			Melting point temperature		
Percentage transformed	T, °K.	Series	Percentage transformed	T, °K.	Series
15	61.55	III	3	68.09	I
45	61.55	III	3	68.07	I
45	61.55	III	20	68.09	II
80	61.55	III	55	68.09	II
80	61.56	III	85	68.09	II
Average	61.55 ± 0.05		Average	68.09 ± 0.05	

In Table III the data of previous observers have been collected.

TABLE III

SUMMARY OF AVAILABLE TRANSITION AND MELTING POINT TEMPERATURE DATA

T, °K.	
Transition Temperature	
60.4	(1916) Eucken[11]
61.51	(1929) Clusius[12]
61.55 ± 0.05	This research
Melting Point	
62	(1877) Cailletet[13]
66	(1885) Olszewsky[14]
74	(1885) Von Wroblewsky[15]
67.3	(1916), Eucken[11]
68.22	(1929) Clusius[12]
68.06	(1931) Verschoyle[16]
68.09 ± 0.05	This research

Purity of Carbon Monoxide.—One of the best methods of estimating an impurity which is soluble in a liquid but insoluble in the solid phase is by calorimetric observation of the premelting effect. The short temperature range of the solid modification stable at the melting point was a slight handicap to this method in the case of carbon monoxide. However, no abnormal rise is apparent in the last point observed below the melting point. The evidence is sufficient to determine that the impurity is not greater than one-thousandth of one mole per cent. The constancy of the melting point confirms the purity although this method is greatly inferior in sensitivity to the premelting method.

Heats of Fusion and Transition.—The heats of fusion and transition were measured by starting the energy input a little below the transition or

[13] Cailletet, *Compt. rend.*, **85**, (1877).

[14] Olszewsky, *ibid.*, **100**, 350 (1885).

[15] Von Wroblewsky, *Wien. Ber.*, **90** (1885).

[16] Verschoyle, *Trans. Roy. Soc.* (London), **A230**, 189 (1931).

fusion temperature, and ending a little above. A correction was made for $\int C_P \, d\,T$. The results are given in Table IV with those of other observers.

TABLE IV

HEATS OF FUSION AND TRANSITION OF CARBON MONOXIDE

Molecular weight 28.000

ΔH transition, Calories per mole	
152.3	Series III
150.4	Series I
151.3 ± 1	(1931) Average this research
144.1	(1916) Eucken[11]
151.2	(1929) Clusius[12]
ΔH fusion	
199.6	Series III
199.7	Series I
199.7	Series II
199.7 ± 0.2	(1931) Average this research
224.1	(1916) Eucken[11]
198.2	(1929) Eucken (corrected by Clusius)[12]
201.5	(1929) Clusius[12]

It may be noticed that the two determinations of the heat of transition differ by an amount far beyond the ordinary limit of our calorimetric error. This point will be considered later.

Vapor Pressures of Solid and Liquid Carbon Monoxide.—Vapor pressures were measured on the same material used in Series II of the calorimetric measurements but not at the same time as it was undesirable to have the manometer volume connected during calorimetric measurements. The apparatus was essentially the same as that described by Giauque, Johnston and Kelley.[17] A Gaertner cathetometer with an accuracy of 0.05 mm. of mercury was used to compare the large diameter manometer with a standard meter.

The results have been represented by equations 1 and 2. For solid carbon monoxide from the transition point at 61.55° to the melting point at 68.09°

$$\log P_{(\text{cm.})} = -\frac{425.1}{T} + 7.82259 - 0.0075960\,T \qquad (1)$$

For liquid carbon monoxide

$$\log P_{(\text{cm.})} = -\frac{477.3}{T} + 11.23721 - 0.064129\,T + 2.5911 \times 10^{-4}\,T^2 \qquad (2)$$

In addition an equation was calculated for the vapor pressure of the solid stable below 61.55°K. This was done with the assistance of the various calorimetric data, including the heat of vaporization to be given below. In correcting the measured heat of vaporization to the value which would be obtained for evaporation to a dilute gas the thermodynamic equation

[17] Giauque, Johnston and Kelley, THIS JOURNAL, 49, 2367 (1927).

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

was combined with Berthelot's equation.

The heat of sublimation of the solid stable at or below 61.55°K. was found to be 1963 calories per mole at 61.55°K. The heat capacity of the solid can be represented very roughly but with sufficient accuracy from 20° to the transition point by

$$C_P = -1.25 + 0.24\ T$$

These several data yield the equation, for solid carbon monoxide below 61.55°K.

$$\log P_{(\text{cm.})} = -\frac{418.2}{T} + 4.127 \log T + 1.47365 - 0.02623\ T \qquad (3)$$

TABLE V

VAPOR PRESSURE OF CARBON MONOXIDE

T, °K. observed	P int. cm. observed	ΔP obs.-calcd.	ΔT obs.-calcd.	Remarks
60.24	1.998	0.019	−0.03	Solid
61.55	2.819			Transition point
	2.810			Transition point
	2.807			Transition point
	2.808			Transition point
	2.810			Transition point
Average	2.811 ± 0.005	0.000	0.00	Transition point
62.22	3.275	− .017	.02	Solid
63.30	4.230	.006	− .01	Solid
64.31	5.283	.008	.01	Solid
65.28	6.546	.013	− .01	Solid
66.12	7.769	− .015	.01	Solid
67.02	9.325	− .019	.01	Solid
68.09	11.529			Melting point
	11.531			Melting point
	11.531			Melting point
Average	11.530 ± 0.005	0.000	0.00	Melting point
69.101	13.651	− .020	.009	Liquid
69.892	15.558	.008	− .003	Liquid
70.690	17.641	− .007	.003	Liquid
72.227	22.364	.040	− .012	Liquid
73.246	25.971	.045	− .012	Liquid
73.860	28.325	.014	− .003	Liquid
74.586	31.347	− .003	.001	Liquid
75.434	35.229	.014	− .003	Liquid
76.351	39.784	− .025	.005	Liquid
77.267	44.859	.002	− .000	Liquid
78.110	49.934	.008	− .001	Liquid
78.948	55.406	− .002	.000	Liquid
79.858	61.871	− .012	.002	Liquid
81.102	71.689	.020	− .002	Liquid
82.032	79.747	− .001	.000	Liquid
83.132	90.206	− .001	.000	Liquid

One observation on the vapor pressure of this modification was made, namely, $P = 1.998$ cm. at 60.24°K. The observed and calculated values are included in Table V. The temperatures at which observations were made on the liquid are given to 0.001 degree as they are relatively consistent to better than 0.01 degree. The principal error appears to be in the pressure measurements, the increase in ΔT, observed–calculated, at the lower temperature, being due largely to this source.

The vapor pressure of carbon monoxide has been measured by Clusius and Teske[18] and their data have been compared with our equations in Table VI.

TABLE VI

VAPOR PRESSURE OF CARBON MONOXIDE

Data of Clusius and Teske Compared with Equations 1 and 2

T, °K. observed	P, int. cm. observed	ΔP obs.–calcd.	ΔT obs.–calcd.	Remarks
60.336	2.041	−0.042	+0.07	Solid
60.616	2.083	− .151	+ .25	Solid
61.455	2.459	− .279	+ .41	Solid
61.985	3.083	− .033	+ .05	Solid
63.974	4.465	− .453	+ .45	Solid
64.348	5.519	+ .179	− .15	Solid
64.892	6.099	+ .090	− .07	Solid
65.967	7.755	+ .215	− .13	Solid
66.201	7.965	+ .051	− .03	Solid
67.171	9.888	+ .255	− .13	Solid
67.373	9.963	− .076	+ .04	Solid
68.213	11.708	− .108	+ .05	Solid
69.735	15.184	+ .023	− .01	Liquid
70.801	17.811	− .146	+ .05	Liquid
71.457	19.795	− .077	+ .03	Liquid
72.338	22.830	+ .135	− .04	Liquid
73.350	26.430	+ .112	− .03	Liquid
73.409	26.521	− .021	+ .01	Liquid
73.994	28.745	− .108	+ .03	Liquid
74.690	31.518	− .285	+ .07	Liquid
74.710	31.897	+ .006	− .00	Liquid
74.778	32.144	− .056	+ .01	Liquid
75.558	35.650	− .160	+ .03	Liquid
75.631	36.180	+ .015	− .00	Liquid
76.004	37.995	− .024	+ .00	Liquid
76.325	39.691	+ .019	− .00	Liquid
76.449	40.783	+ .457	− .08	Liquid
76.574	40.878	− .006	+ .02	Liquid
77.497	46.482	+ .286	− .05	Liquid
77.499	46.492	+ .283	− .05	Liquid
78.265	51.062	+ .154	− .02	Liquid
78.828	54.620	+ .024	− .00	Liquid
79.696	60.666	− .022	+ .00	Liquid
79.967	62.418	− .278	+ .04	Liquid

[18] Clusius and Teske, *Z. physik. Chem.*, [B] **6**, 135 (1929).

While the average deviation is very much greater than in the present work, the results are well represented by our equations. In fact, equation 1 represents the data of Clusius and Teske for the liquid range with a slightly smaller average deviation than was obtained with their own equation.[19]

From equation 1 the boiling point was found to be 81.61 ± 0.05°K. The boiling point data of several observers are summarized in Table VII.

TABLE VII

BOILING POINT OF CARBON MONOXIDE

T, °K.	Observer
80	(1885) Von Wroblewsky[20]
83	(1885) Olszewsky[14]
81.8	(1902) Baly and Donnan[5]
81.66	(1919) Von Winning (corrected to Leiden scale)[18]
81.62	(1929) Clusius and Teske[18]
81.62	(1931) Verschoyle[16]
81.61 ± 0.05	This research

Heat of Vaporization of Carbon Monoxide.—The entropy of vaporization contributes roughly one-half of the total entropy for the simple gases. For this reason it is very desirable to have a direct and accurate determination of this quantity. The experimental method has been described previously.[2,3]

The results are given in Table VIII, which also includes the value given by Eucken and that calculated from our vapor pressure determinations. The latter method is in general inferior to the directly determined value due to uncertain correction for gas imperfection at the higher pressures and to increasing error in dP/dT at low pressures.

[19] Since this paper was written our attention has been called to some very accurate vapor pressure measurements by Verschoyle [*Trans. Roy. Soc.* (London), **A230**, 189 (1931)]. The equation given by Verschoyle does not represent his values in the liquid range, the discrepancy undoubtedly being due to some typographical error. However, we have compared his results from the melting point to 82.2° with our Equation 2. The agreement is extraordinarily good. The maximum deviation is 0.02° and the average deviation 0.01°. However, Verschoyle's results, which extend to a pressure of 143 cm., are not very satisfactorily represented by our Equation 2 above the boiling point. Below the melting point the agreement is not as good. Although Verschoyle's results extend to 54.21°K., he apparently failed to notice the transition at 61.55°K. and represents all of his results on the solid states by a single equation. Near the transition temperature Verschoyle's temperatures are about 0.06° higher than the present work. Below 61.55°K. Verschoyle's results do not agree well with our equation 3 obtained with the assistance of the calorimetric data. At 54.2°K. his results are 0.12° lower than those given by Equation 3. However, our one observation on this crystal modification at 60.24° is only 0.03° lower than Verschoyle's results in this region.

For comparison: Boiling point, 81.62° (V.), 81.61° (C. and G.).
Triple point temperature, 68.06° (V.), 68.09° (C. and G.).
Triple point pressure, 11.486 cm. (V.), 11.531 cm. (C. and G.).

[20] Von Wroblewsky, *Compt. rend.*, **100**, 979 (1885).

TABLE VIII

HEAT OF VAPORIZATION OF CARBON MONOXIDE

Molecular weight 28.000

ΔH at 760 mm. in cal./mole	Moles of CO evaporated	Time in minutes	Remarks
1443.4	0.22487	36	Series II
1444.1	.21939	46	Series I
1444.8	.21934	46	Series I
1442.6	.21913	46	Series I
1442.8	.21979	46	Series I
1443.6 ± 1.0 average	This research		
1414	Eucken (1916)[11]		
1434	From vapor pressure equation 2, assuming a Berthelot gas		

The 1434 value for the heat of vaporization obtained from the vapor pressure measurements is of course to be given no weight in comparison with the calorimetric value. This calculation, however, increases the justification for assuming that Berthelot's equation represents the behavior of carbon monoxide. This will be assumed later in connection with the effect of gas imperfection on the entropy.

The Entropy of Carbon Monoxide.—The entropy calculation is summarized in Table IX. A Debye function with $h\nu/k = 79.5$ was used to extrapolate to the absolute zero.

TABLE IX

CALCULATION OF ENTROPY OF CARBON MONOXIDE

0–11.70°K. Debye extrapolation $h\nu/k = 79.5$	0.458
11.70–61.55 Graphical	9.632
Transition 151.3/61.55	2.457
61.55–68.09 Graphical	1.228
Fusion 199.7/68.09	2.933
68.09–81.61 Graphical	2.611
Vaporization 1443.6/81.61	17.689
Entropy of carbon monoxide gas at boiling point	37.01 ± 0.1
Correction for gas imperfection assuming Berthelot gas	0.21
Entropy corrected to the ideal state	37.2 E. U.

The 0.21 E. U. correction for gas imperfection was calculated by combining Berthelot's equation with the thermodynamic equation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \text{ yielding}$$

$$\Delta S_{\text{correction}} = R\frac{27\ T_c^3 P}{32\ T^3 P_c}$$

The critical data were taken from the review of such data given by Pickering[21]

$$T_c = 134.1°\text{K.} \quad P_c = 35 \text{ atmospheres}$$

[21] Pickering, *Sci. Papers Bur. Standards*, **21**, 608 (1926).

The correction to the ideal state is necessary in order that comparison may be made with the entropy which will now be calculated from the band spectrum of carbon monoxide.

The entropy is given by the expression

$$S^\circ = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P - \frac{5}{2}R - 7.267 + R\ln Q + RT\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \qquad (4)^{22}$$

$$Q = \Sigma p e^{-\epsilon/kT} \text{ over all quantum levels}$$

The energy levels of carbon monoxide may be represented by the expressions

$$\epsilon_{\text{rotation}} = [B_e + \alpha(v + 1/2)]m^2 + [D_e + \beta(v + 1/2)]m^4$$
$$\epsilon_{\text{vibration}} = \omega_e(v + 1/2) + \omega_e X_e (v + 1/2)^2$$

Birge[23] has recalculated the data of Snow and Rideal[24] and gives $B_e = 1.853$, $\alpha = 0.020$, $D_e = 5.418 \times 10^{-6}$, $\beta = -6.918 \times 10^{-8}$, $\omega_e = 2167.4$, $\omega_e X_e = -12.70$. Mulholland[25] has expressed Q as a simple series in terms of B for rigid molecules. Giauque and Overstreet[26] have given an expression which is suitable for non-rigid molecules.

$$Q = e^{\frac{hc}{kT}\left(\frac{B}{4} + \frac{D}{16}\right)} \cdot \frac{kT}{Bhc}\left[1 + \frac{B}{12}\left(\frac{hc}{kT}\right) - \frac{2D}{B^2}\left(\frac{kT}{hc}\right) + \frac{12D^2}{B^4}\left(\frac{kT}{hc}\right)^2 + \ldots\ldots\right] \qquad (5)$$

This avoids the considerable labor involved in summing the individual Boltzmann factors for the rotational levels.

From the above expression for Q and the derivative of its logarithm used in equation 4, the entropy of carbon monoxide is calculated and given in Table X. The values for all natural constants are those given in the "International Critical Tables."

TABLE X

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC ENTROPIES OF CARBON MONOXIDE

		Experimental	
T, °K.	Spectroscopic	Actual gas	Corrected to ideal state
81.61	38.318	37.0 ± 0.1	37.2 E. U.
298.1	47.313	.....	46.2

The "experimental" value given for 298.1°K. was obtained by adding the calculated increase in column 2 to 37.2.

It is clear from the discrepancy between the spectroscopic and experimental values that some random situation remains in the solid state at liquid hydrogen temperatures. This is in addition to the small amount considered by the Debye extrapolation.

The difference between the two values is roughly $R\ln 2$. We believe that

[22] Giauque, THIS JOURNAL, **52**, 4808 (1930).

[23] Birge, Personal communication.

[24] Snow and Rideal, *Proc. Roy. Soc.* (London), **A125**, 462 (1929).

[25] Mulholland, *Proc. Cambridge Phil. Soc.*, **24**, 280 (1928).

[26] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

the discrepancy arises as follows. If we consider a molecule with two or more otherwise equivalent positions occupied by isotopes of a given element, it is found that such a molecule enters a crystal lattice without any particular isotopic preference. However, it is true that at extremely low temperatures the almost negligible but nevertheless real energy differences between the possible arrangements will become comparable with kT and thus the crystal will attain perfect order on *reversible* approach to the absolute zero. It is evident even when the positions are occupied by different elements that, unless the crystal lattice has a sufficiently strong preference for a certain arrangement to impose an energy difference much larger than kT, the several possible orientations will exist. It is suggested that this is the case in solid carbon monoxide. This seems more probable when one considers the similar atomic sizes and that it has frequently been assumed that carbon monoxide has an electron structure similar to nitrogen. A discussion of this point has been given by Lewis.[27]

The electron structure, symmetrical in nitrogen, would of course be somewhat deformed by the differing charges on the carbon and oxygen kernels. Nevertheless, it seems entirely reasonable to assume that the polarity thus induced is insufficient to fix the carbon and oxygen atoms in definite positions at the temperature where the solid is formed. It appears that orderly arrangement in the above respect occurs in carbon monoxide below the temperatures investigated or, what is still more probable, that rearrangement to equilibrium is not easily possible in the solid. In this connection it may be recalled that two determinations of the heat of transition given in Table IV differed by an amount considerably beyond the ordinary limit of error. While no definite conclusion is possible, the difference could be attributed to a different degree of approach to equilibrium in the solid stable below 61.55°K. Unfortunately the experiments were concluded before the calorimetric calculations yielded this information. It would be interesting to hold carbon monoxide at various temperatures below 61.55° for considerable periods of time to investigate this effect.

The amount of entropy corresponding to a complete lack of discrimination between the carbon and oxygen ends of the molecule is $R \ln 2 = 1.38$ E. U. The fact that the observed discrepancy is somewhat smaller, namely, 1.1 E. U., indicates also that some approach to order has been made and that inability to obtain equilibrium is a factor.

The above type of difficulty, while possible only in certain special cases, is perhaps the most perplexing feature that has been encountered in the practical application of the third law of thermodynamics. It is perplexing because it is by no means obvious how we are to know when it exists. The crystal under investigation may appear perfect to our present powers of

[27] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, p. 126.

observation, including x-rays and yet the effect may be present. Certain types of organic molecules would appear to be susceptible to this effect.

The Free Energy of Carbon Monoxide.—From the expression[22]

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2} R \ln M - \frac{5}{2} R \ln T + R \ln P + 7.267 - R \ln Q$$

and the band spectra data previously given, the values of $(F^\circ - E_0^\circ)/T$ have been calculated. The value of R was taken as 1.9869 calories per degree per mole. The results are given in Table XI. The values given in heavy type have been directly calculated. The others have been interpolated by means of a difference plot making use of the Einstein harmonic oscillator function.

TABLE XI

$(F^\circ - E_0^\circ)/T$ FOR CARBON MONOXIDE

T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
250	**39.138**	1200	50.199	3100	57.773
298.1	**40.361**	1250	50.502	3200	57.832
300	**40.405**	1300	50.793	3300	58.083
350	41.476	1400	51.347	3400	58.328
400	**42.404**	1500	**51.867**	3500	**58.566**
450	43.224	1600	52.356	3600	58.798
500	**43.959**	1700	52.819	3700	59.024
550	44.624	1800	53.259	3800	59.245
600	45.233	1900	53.678	3900	59.461
650	45.791	2000	**54.077**	4000	**59.671**
700	46.317	2100	54.458	4100	59.867
750	**46.806**	2200	54.824	4200	60 077
800	47.264	2300	55.176	4300	60.274
850	47.696	2400	55.513	4400	60.466
900	48.106	2500	**55.838**	4500	**60.655**
950	48.495	2600	56.152	4600	60.839
1000	**48.867**	2700	56.455	4700	61.020
1050	49.221	2800	56.748	4800	61.197
1100	49.560	2900	57.031	4900	61.372
1150	49.886	3000	**57.307**	5000	**61.542**

Before considering the reaction

$$C_{graphite} + 1/2\ O_2 = CO$$

it is necessary to obtain the $(F^\circ - E_0^\circ)/T$ for graphite. The values for oxygen have been tabulated by Johnston and Walker.[28]

The calculation for graphite was made graphically, using the heat capacity data collected in the "I. C. T." These data extend only to 2400°K. and are not as accurate as might be desired. However, it can be seen, by analogy with other substances, that the heat capacity curve given by the available data is not likely to be much in error. The values ob-

[28] Johnston and Walker, have kindly allowed us to use their data in advance of publication.

tained are given in Table XII. The values for graphite have been expressed to 0.001 unit although this is considerably beyond the absolute accuracy of the heat capacity data. This is in accordance with the free energy convention which thus allows accurate differences to be obtained.

TABLE XII

$(F^\circ - E_0^\circ)/T$ FOR GRAPHITE

T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
250	0.403	850	2.325	1800	4.941
298.1	.545	900	2.485	1900	5.172
300	.551	950	2.643	2000	5.394
350	.698	1000	2.798	2100	5.608
400	.854	1050	2.950	2200	5.817
450	1.016	1100	3.099	2300	6.021
500	1.180	1150	3.246	2400	6.218
550	1.345	1200	3.391	2500	6.411
600	1.510	1250	3.534	2600	6.600
650	1.674	1300	3.674	2700	6.783
700	1.838	1400	3.945	2800	6.962
750	2.001	1500	4.206	2900	7.137
800	2.164	1600	4.460	3000	7.309
		1700	4.704		

$$\frac{\Delta F}{T} = -R \ln K = \Delta\left(\frac{F^\circ - E_0^\circ}{T}\right) + \Delta E_0^\circ \qquad (6)$$

ΔE_0° is given by the equation

$$\Delta E_0^\circ = \Delta H^\circ - \left[\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right]_{CO} + {}^1/_2\left[\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right]_{O_2} + [H^\circ - E_0^\circ]_C \qquad (7)$$

The value of ΔH° was obtained by difference of the heats of combustion of graphite and of carbon monoxide.

For the first of these the value of Roth and Naeser[29] was adopted. We have learned from Professor G. S. Parks that a personal communication from Professor Roth states that the graphite weighings were not given on a vacuum basis. The application of the correction for buoyancy leads to a value of 94,240 as the heat of combustion of 12.000 g. of β graphite at 298.1°K.

For the second, the work of Rossini[30] gives 67,623 ± 30 calories as the heat of combustion of carbon monoxide at 298.1°K.

Combining

$$C_{(\beta\ \text{graphite})} + {}^1/_2O_2 = CO \quad \Delta H^\circ_{298.1} = -26{,}620$$

For carbon monoxide

$$\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} = 1480.7 + 590.2$$
$$= 2070.9 \text{ calories at } 298.1\,^\circ\text{K.}$$

[29] Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925).

[30] Rossini, *Bur. Standards J. Research*, **6**, 37 (1931).

For oxygen

$$\frac{1}{2}\left[\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right] = \frac{1}{2}[1480.7 + 589.6]$$
$$= 1035.2 \text{ calories at } 298.1\,^\circ\text{K.}$$

For graphite the "I. C. T." give

$$H^\circ - E_0^\circ = 251.4 \text{ calories at } 298.1\,^\circ\text{K.}$$

Combining the several values in equation 7, $\Delta E_0^\circ = -27{,}404$ calories per mole of carbon monoxide.

TABLE XIII

FREE ENERGY OF FORMATION OF CARBON MONOXIDE

T, °K.	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$-\frac{\Delta F^\circ}{T}$	$K = [CO]/[O_2]^{1/2}$
298.1	18.776	110.705	1.58×10^{24}
300	18.792	110.139	1.19×10^{24}
350	19.182	97.479	2.03×10^{21}
400	19.487	87.997	1.71×10^{19}
450	19.733	80.631	4.21×10^{17}
500	19.933	74.746	2.17×10^{16}
550	20.096	69.921	1.92×10^{15}
600	20.231	65.904	2.54×10^{14}
650	20.339	62.499	4.58×10^{13}
700	20.435	59.584	1.06×10^{13}
750	20.510	57.049	2.95×10^{12}
800	20.570	54.825	9.64×10^{11}
850	20.619	52.859	3.58×10^{11}
900	20.657	51.106	1.48×10^{11}
950	20.687	49.533	6.71×10^{10}
1000	20.713	48.117	3.29×10^{10}
1050	20.732	46.831	1.72×10^{10}
1100	20.747	45.660	9.55×10^{9}
1150	20.757	44.587	5.57×10^{9}
1200	20.763	43.600	3.39×10^{9}
1250	20.766	42.689	2.14×10^{9}
1300	20.766	41.846	1.40×10^{9}
1400	20.762	40.336	6.56×10^{8}
1500	20.751	39.020	3.38×10^{8}
1600	20.733	37.861	1.89×10^{8}
1700	20.712	36.832	1.13×10^{8}
1800	20.688	35.912	7.08×10^{7}
1900	20.659	35.082	4.66×10^{7}
2000	20.629	34.331	3.19×10^{7}
2100	20.599	33.649	2.26×10^{7}
2200	20.568	33.024	1.65×10^{7}
2300	20.534	32.449	1.24×10^{7}
2400	20.500	31.918	9.48×10^{6}
2500	20.465	31.427	7.40×10^{6}
2600	20.428	30.968	5.88×10^{6}
2700	20.392	30.542	4.74×10^{6}
2800	20.355	30.142	3.87×10^{6}
2900	20.317	29.767	3.21×10^{6}
3000	20.279	29.414	2.69×10^{6}

From this value, the several values of $(F^\circ - E_0^\circ)/T$ and equation 6, $\Delta F^\circ/T$ and K have been computed for the formation of carbon monoxide from the elements. The results are given in Table XIII.

The values of K should be accurate to about 5%. At the lower temperatures the error is chiefly in ΔE_0° and at the higher temperatures the uncertainty is almost entirely due to the data on graphite.

In the absence of better information on the heat capacity of carbon above 3000° it seems preferable to omit values above 3000°. However, the values for carbon monoxide have been extended to 5000° and the values for $(F^\circ - E_0^\circ)/T$ of oxygen given by Johnston and Walker[28] extend to this temperature. Thus by extrapolation of the data for graphite above 3000°K. a quite reliable calculation of the equilibrium is available.

We wish to thank H. L. Johnston for assisting with the measurements of series I and R. W. Blue for assisting with series II and III.

Summary

The heat capacities of the two crystalline forms of carbon monoxide and the liquid have been measured from 13°K. to the boiling point.

The transition temperature was found to be 61.55°K. ± 0.05, the melting point 68.09°K. ± 0.05 and the boiling point 81.61°K. ± 0.05. From the calorimetric measurements the heat of transition was determined as 151.3 ± 1 calories per mole, the heat of fusion 199.7 ± 0.2 and the heat of vaporization 1443.6 ± 1.0 calories per mole, measured at 760 mm.

From the experimental data the entropy of carbon monoxide gas was calculated to be 37.0 ± 0.1 E. U. at 81.61°K. Assuming Berthelot's gas equation a correction amounting to 0.2 E. U. for gas imperfection was added, giving 37.2 E. U. This value can be compared to the value calculated for the ideal gas from the band spectrum, 38.318 at 81.61°K.

The observed entropy is low by an amount corresponding approximately to $R \ln 2$. Reasons are given for believing that this is due to lack of discrimination within the crystal lattice for the oxygen and carbon ends of the molecule. It is suggested that this effect may exist in other molecules and that a quantitative correction will be possible in many cases.

The entropy of carbon monoxide gas at 298.1°K. was found to be 47.313 E. U. from the band spectrum data.

The vapor pressure of solid and liquid carbon monoxide was measured and represented by the equations

Liquid 68.09° – 83.13°K.

$$\log P(\text{cm.}) = -\frac{477.3}{T} + 11.23721 - 0.064129\ T + 2.5911 \times 10^{-4}\ T^2$$

Solid 61.55° – 68.09°K.

$$\log P(\text{cm.}) = -\frac{425.1}{T} + 7.82259 - 0.0075960\ T$$

Solid below 61.55°K.

$$\log P(\text{cm.}) = -\frac{418.2}{T} + 4.127 \log T + 1.47365 - 0.02623\ T$$

The free energy function for carbon monoxide was calculated from spectroscopic data and tabulated to 5000°K. These data were combined with similar data on oxygen and with the available calorimetric data on graphite to give ΔF for the reaction $C_{graphite} + {}^1/_2O_2 = CO$ to 3000°K.

The free energy of formation of carbon monoxide from β graphite and oxygen at 298.1°K. was found to be $\Delta F^\circ_{298.1} = -33{,}000$.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION FROM BOILING POINT DATA[1]

BY BLAIR SAXTON AND RODNEY P. SMITH

RECEIVED JANUARY 18, 1932 PUBLISHED JULY 6, 1932

Although the thermodynamic properties of aqueous salt solutions at ordinary temperatures have been extensively investigated, few data are available for the study of these properties at higher temperatures. Measurements of the boiling point elevation of solutions could be used for such a study if sufficient accuracy in the measurement could be attained. Considerable data[2] have been published on the boiling point elevation of salt solutions. However, due to superheating, variation of pressure, errors of analysis or temperature measurement, the results are not of sufficient accuracy for a calculation of the activity coefficient. It has seemed worth while, therefore, to attempt to design an apparatus for a more accurate determination of the boiling point elevation.

Apparatus

Of the different methods used for the elimination of superheating, the one suggested by Cottrell[3] and used by Washburn and Read,[4] Pearce and Hicks,[5] and Bancroft and Davis[6] seems to be the most satisfactory.

The first apparatus, Fig. 1, consisted of a Pyrex tube, A, 43 cm. long and 7.6 cm. inside diameter, over which was sealed a larger tube, B, 28 cm. long, 11.5 cm. inside diameter. A condenser, C, and a small drain tube, D, were sealed into the outer tube, B. A tube, E, for the "cold" junction of the thermocouple was also sealed into the

[1] Part of this paper is from a dissertation submitted by Rodney P. Smith to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] For summary of results see "International Critical Tables," Vol. III, p. 324.

[3] Cottrell, THIS JOURNAL, **41**, 721 (1919).

[4] Washburn and Read, *ibid.*, **41**, 729 (1919).

[5] Pearce and Hicks, *J. Phys. Chem.*, **30**, 1678 (1926).

[6] Bancroft and Davis, *ibid.*, **33**, 591 (1929).

outer tube, B. (For all but the dilute solutions, however, it was found that the cold junction was affected by the temperature of the solution tube, thus necessitating the use of an outside hypsometer.) The solution tube, G, fitted into the ground opening, F. A ground-glass stopper carried a tube, J, for the hot junction of the thermocouple, and two small tubes, I, for the lead-wires to the platinum heating coil. The heating coil was of No. 22 wire and had a resistance of about 0.04 ohm. The seal through the lead-wire tubes was made with heavy tungsten wire, the platinum wire being soldered to the tungsten with hard silver solder. Contact between the lead wires and the tungsten was made with mercury. The lead-wires were of sufficient size to carry 20 to 25 amperes without heating. A Cottrell pump, L, was fixed in the center of the solution tube. Samples for analysis were withdrawn through a large capillary tube, N. The pure solvent in the outer tube was heated with a gas flame. The entire apparatus was protected from air currents by a transite box.

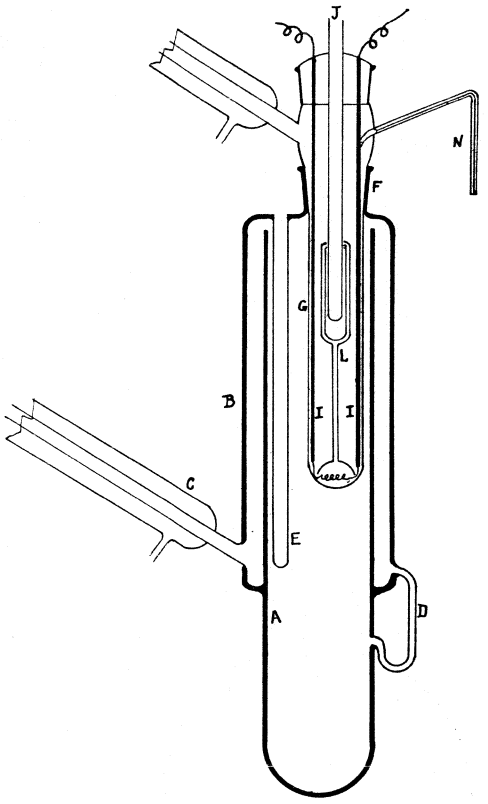


Fig. 1.

The apparatus has the advantages of electric heating and the Cottrell pump as a means of eliminating superheating. Since the solution is heated nearly to its boiling point by the vapor of the pure solvent, only a small amount of heat is required from the electric heating coil. Thus, it is possible to boil the solution with a drop of potential across the heating coil below the decomposition potential of the solution. A small transformer was used as a source of current for the heating coil.

A 20-junction No. 36 copper–No. 30 constantan thermocouple, constructed according to the specification of White,[7] was used to measure the elevations. The thermocouple was calibrated from the following fixed points: freezing point of mercury, transition point of sodium sulfate, transition point of manganous chloride, boiling point of water and boiling point of naphthalene. The e. m. f. of the thermocouple was measured with a shielded Leeds and Northrup type K potentiometer.

The pressure was maintained constant to less than 0.1 mm. by an apparatus similar to that described by Carroll, Rollefson and Mathews.[8]

The degree of superheating was found to be zero by using pure water, both in the inside and in the outer tubes. The accuracy of this apparatus was found to be 0.0025°.

With the Cottrell pump it is not possible to raise the solution very high above the surface of the liquid; therefore, unless the end of the thermocouple tube is near the surface of the liquid, its immersion depth is not very great. Due to the large heat con-

[7] White, THIS JOURNAL, **36**, 2292, 2313 (1914).

[8] Carroll, Rollefson and Mathews, *ibid.*, **47**, 1791 (1925).

ductivity of multi-junction thermocouples, there is the danger that the observed elevations are too low. With the view of eliminating this possible error, a second apparatus, shown in Fig. 2, was designed. The solution tube consisted of a two-liter Pyrex round-bottomed flask, connected through a ground-glass stopper to an upper chamber, B, by three tubes, C, D and E. The tube, F, for the thermocouple was sealed in the center of the upper chamber, B. By partially closing the stopcock in tube C, a slight pressure was developed in the solution flask, causing the solution to rise slightly in the tube E; vapor was allowed to pass into the tube E through a pinhole, G. The vapor, in rising through the tube E, carried small amounts of solution with it, thus causing an intimate mixture of liquid and vapor to squirt continuously over the thermocouple tube, F. With this arrangement, the immersion depth of the thermocouple was more than doubled. The tube D served to return the solution to the solution flask. Samples for analysis were withdrawn through the tube H. Since the volume of the solution used with this apparatus was relatively large, it was possible to draw off samples for analysis of 100 to 150 cc., thus decreasing the error due to evaporation while the sample was being taken.

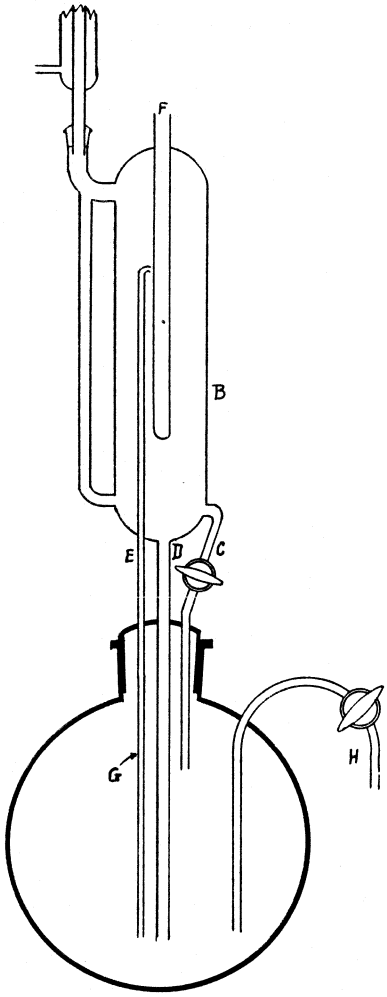


Fig. 2.

The "cold" junction of the thermocouple was in another apparatus of exactly similar design. The entire apparatus was enclosed in an insulating box. Gas flames were used as a source of heat.

A 26-junction copper–constantan thermocouple, calibrated against a standard platinum resistance thermometer with a Bureau of Standards certificate, was used with this apparatus.

Readings constant to 0.0005° could be obtained over time periods of about an hour; however, due to some error which we were not able to eliminate, readings over longer periods of time may vary as much as 0.0015°.

Theory.—The theory of the calculation of the activity coefficient of a non-volatile strong electrolyte from the boiling point of the solution is identical with that developed by Lewis and Randall[9] for the case of freezing point lowering, the proper changes having been made. Taking the pure liquid solvent as the standard state and expressing T as $T_0 + \theta$, where T_0 is the boiling point of the pure solvent and θ is the elevation of the boiling point; and expressing ΔH as $\Delta H_{(T_0)} + \Delta C_p\theta$, where

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 282 ff.

$\Delta H_{(T_0)}$ is the molal heat of vaporization of the pure solvent at its boiling point and ΔC_p is the molal increase in heat capacity of the pure solvent on vaporization, we obtain

$$d \ln a_1' = -\frac{d\theta}{RT_0^2}\left[\Delta H_{(T_0)} - \left(\frac{2\Delta H_{(T_0)}}{T_0} - \Delta C_p\right)\theta + \left(\frac{3\Delta H_{(T_0)}}{T_0^2} - \frac{2\Delta C_p}{T_0}\right)\theta^2 + \ldots.\right] \quad (1)$$

Using the values given in Volume 5 of the "International Critical Tables," we obtain

$$\begin{aligned} \Delta H_{(T_0)} &= 40.679 \text{ j. mole}^{-1}\ ^{10a} \\ C_{p(l)} &= 75.72 \text{ j. mole}^{-1}\ ^{10b} \\ C_{p(v)} &= 36.34 \text{ j. mole}^{-1}\ ^{10c} \\ \Delta C_p &= -39.38 \text{ j. mole}^{-1} \end{aligned}$$

Hence, taking T_0 as 373.1° and R as 8.315 j. mole^{-1} degree^{-1}

$$d \ln a_1' = (-0.03514 + 0.0002224\,\theta + \ldots.)\, d\theta \quad (2)$$

where a_1' is the activity of the solvent at the boiling point of the solution. The geometrical mean activity of a solute completely dissociated into ν ions is then given by

$$d \ln a_{\pm}' = \frac{d\theta}{\nu\lambda m} - 0.01235\frac{\theta d\theta}{\nu m} \quad (3)$$

where m is the molality of the solute and $\lambda = d\theta/dm$ at infinite dilution. Hence, $\lambda = 1/55.508 \times 0.03514 = 0.5126$.[11] The mean activity coefficient of the solute at the boiling point of the solution is given by

$$d \ln \gamma' = -dj - \frac{j}{m}dm - \frac{0.01235}{\nu}\frac{\theta}{m}d\theta \quad (4)$$

where j, which is equal to one minus Φ, the osmotic coefficient of Bjerrum,[12] is defined as in Lewis and Randall[13] by the equation

$$j = 1 - \frac{\theta/m}{\nu\lambda}$$

Integration of equation (4) gives the equation

$$\log \gamma' = -0.4343\, j - 0.4343\int_0^m \frac{j}{m}dm - \frac{0.00536}{\nu}\int_0^m \frac{\theta}{m}d\theta \quad (5)$$

These equations differ from that used by Cann and Gilmore[14] in that our value of λ is slightly lower and in accord with that given by Randall[15] (0.5125), but particularly in the numerical coefficient of the last term of the equation. We differ in sign and magnitude. Apparently they have used a value identical with that given by Lewis and Randall for freezing point

[10] "International Critical Tables," Vol. V, p. (a) 138, (b) 113, (c) 82.

[11] This value varies slightly with the barometric pressure. See Washburn and Read, THIS JOURNAL, **41**, 729 (1919).

[12] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

[13] Lewis and Randall, Ref. 9, p. 347.

[14] Cann and Gilmore, *J. Phys. Chem.*, **32**, 72 (1928).

[15] Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

lowering. It is quite obvious that their value is wrong in both sign and magnitude since, for the boiling point, $dT = d\theta$, and the coefficient contains both $\Delta H_{(T_0)}$ and ΔC_p.

Since the last integral in equation (5) is relatively small, it offers no difficulty and is evaluated graphically as usual. The first integral, however, requires that accurate values of j be obtained in very dilute solutions in order that it be similarly treated. This is more difficult to accomplish than it is with the freezing point method, due mainly to the facts that λ is smaller and that it is more difficult to obtain true equilibrium between solution and saturated vapor than it is between solution and ice. We have, therefore, used the Debye–Hückel theory in dealing with the dilute solutions.

In sufficiently dilute solutions the activity coefficient may be calculated by means of the equation of Debye and Hückel; hence, we may write

$$\ln \gamma = \frac{-k\sqrt{c}}{1 + A\sqrt{c}}$$

where c is the concentration in moles of solute per liter of solution and in dilute solutions may be set equal to m, the molality of the solution, times d, the density of the pure solvent. At 100° the error in $\sqrt{c}$ at 0.1 m thus introduced is only 0.1%. Making this substitution, we obtain

$$\ln \gamma = \frac{-k\sqrt{d}\sqrt{m}}{1 + A\sqrt{d}\sqrt{m}}$$

At 25° this equation expresses the activity coefficient of potassium chloride up to 0.1 m within the accuracy of our measurements. The value of A is, however, different from the value obtained if the equation of Hückel[16] be used. Taking the density of water at 100° as 0.9584,[17] we may write

$$\ln \gamma = \frac{-0.9790\, k\sqrt{m}}{1 + 0.9790\, A\sqrt{m}} = \frac{-k'\sqrt{m}}{1 + A'\sqrt{m}} \qquad (6)$$

Differentiating, and equating the differential to the first two terms in equation (4), we obtain

$$d(mj) = \frac{k'\sqrt{m}\, dm}{2(1 + A'\sqrt{m})^2}$$

Then

$$j = \frac{k'}{(A')^3 m}\left[1 + A'\sqrt{m} - 2\ln(1 + A'\sqrt{m}) - \frac{1}{1 + A'\sqrt{m}}\right] \qquad (7)$$

or

$$j = k'\left[\frac{1}{3}m^{1/2} - \frac{2}{4}A'm^{2/2} + \frac{3}{5}(A')^2 m^{3/2} \ldots\ldots\right]$$
$$= -k'\sum_{n=1}^{n=\infty}(-1)^n \frac{n}{n+2}(A')^{n-1} m^{n/2} \qquad (8)$$

[16] Hückel, *Physik. Z.*, **26**, 93 (1925).

[17] "International Critical Tables," Vol. III, p. 26.

For a uni-univalent strong electrolyte, equation (7) is practically identical with equation (53) of Debye and Hückel[17a] which they obtained in a different manner. The limiting law of Debye and Hückel has been used in the calculation of j for dilute aqueous solutions near the freezing point by Debye and Hückel[17a] and by Scatchard.[18] Gronwall, La Mer and Sandved,[18a] in their equation (113), give, for strong electrolytes of the symmetrical valence type, the additions to the equation for j which result from considering the higher terms of the Debye–Hückel theory, while the corresponding expression for unsymmetrical electrolytes is given by La Mer, Gronwall and Greiff[18b] in their equation (9). The application to freezing point depression is discussed in each paper. We do not believe the accuracy of our data warrants our use of the "Extended Theory."

From equation (8) the limiting value of $j/\sqrt{m}$ at 100° becomes $k'/3$. Randall[19] has made similar calculations of this limit for lower temperatures.

From equation (7) or (8), the dielectric constant of water at 100°, and an accurate value of j in dilute solution, the value of A' can be calculated and all the values of j and of the first integral of equation (5) can be computed up to $m = 0.1$, or the values of γ for the dilute solutions can be computed, using equation (6). The integration can be performed either graphically or analytically. We have used the latter method, which gives

$$\int_0^m \frac{j}{m}\,dm = \frac{k'}{A'}\left[\frac{2\ln(1 + A'\sqrt{m})}{(A')^2 m} - \frac{2}{A'\sqrt{m}} + 1\right] \tag{9}$$

or

$$\int_0^m \frac{j}{m}\,dm = k'\left[\frac{2}{3}m^{1/2} - \frac{2}{4}A'm^{3/2} + \frac{2}{5}(A')^2 m^{3/2}\ldots\ldots\right] = -k'\sum_{n=1}^{n=\infty}(-1)^n \frac{2}{n+2}(A')^{n-1}m^{n/2} \tag{10}$$

In Table I this is referred to as Method I.

An alternate method which places less weight on a single value of j can be developed by integrating equation (4) between limits, the lower of which is an arbitrarily fixed value of the molality, m_0. This gives

$$\log \gamma' = \log \gamma'_{m_0} + 0.4343\, j_{m_0} - 0.4343\, j - 0.4343 \int_{m_0}^{m} \frac{j}{m}\,dm - 0.00268 \int_{m_0}^{m} \frac{\theta}{m}\,d\theta \tag{11}$$

Since the correction of γ' to 100° is small even in fairly concentrated solutions, we may evaluate $\log \gamma'$ by means of the equation of Hückel[16]

$$\log \gamma = \frac{-0.4343\, k\sqrt{c}}{1 + A\sqrt{c}} + Bc - \log(1 + 0.036\, m)$$

[17a] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[18] Scatchard, THIS JOURNAL, **47**, 648 (1925).

[18a] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[18b] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

[19] Randall, THIS JOURNAL, **48**, 2512 (1926).

Combining the first two terms on the right side of equation (11) into a constant, C, we then have

$$-\frac{0.4343\,k\sqrt{c}}{1+A\sqrt{c}}+Bc-\log(1+0.036\,m)=C-0.4343\,j-0.4343\int_{m_0}^{m}\frac{j}{m}\,dm-0.00268\int_{m_0}^{m}\frac{\theta}{m}\,d\theta \quad (12)$$

The integrals can be evaluated graphically, k can be calculated from the dielectric constant for water at 100°; hence the constants A, B and C can be determined by solving three such equations simultaneously. The activity coefficients at 0.1 molal or at m_0 and the lower concentrations can then be calculated by using Hückel's equation. In Table I this is called Method II.

The dielectric constant of water has been measured near 100° by Kockel[20] and Wyman.[21] The average of their results for 100° is 55.3. Using this value, 0.4343 k becomes 0.612, k' becomes 1.380 and the limiting value of $j/\sqrt{m}$ becomes 0.460.

Experimental Results

The observed values of θ were first plotted against m on a large scale, giving greater weight to the results obtained with the second apparatus. The values of θ read from the plot are given in Table II. Values of j were then calculated and plotted against m on a large scale, giving the values in Table II. The original data are plotted in Fig. 3 in a manner which has been used by Randall[22] for freezing point and vapor pressure data. The values of j used in Table II are identical with those read from this curve. Values of $\gamma_{0.1}$ were then calculated by the two methods described above. The results are given in Table I.

TABLE I

Method I

m	j	k'	A'	$\gamma_{0.1}$
0.1	0.082	1.380	1.44	0.741

Method II

m_0	m_1	m_2	m_3	A	B	$\gamma_{0.1}$
0.1	0.2	1.0	2.0	1.22	0.042	0.733
.2	.5	1.0	2.0	1.13	.046	.729

The average value of $\gamma_{0.1} = 0.731$ obtained by the second method agrees with that calculated from the value of $\gamma_{0.1}$ at 25° (see Table IV); hence, we have taken it as our reference value. If it be substituted in equation (6), A' becomes 1.24 and this equation was then used to compute the

[20] Kockel, *Ann. Physik*, [4] **77**, 417 (1925).

[21] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[22] (a) Randall, THIS JOURNAL, **48**, 2512 (1926); (b) Randall and White, *ibid.*, **48**, 2514 (1926).

activity coefficients of the more dilute solutions. The values so found are identical with those obtained by using the equation of Hückel with $A = 1.18$ and $B = 0.044$, the averages of the values given in Table I. The activity coefficients of these dilute solutions are included in Table II. The value of the integral from $m = 0$ to $m = 0.1$ was then calculated from $\gamma_{0.1}$ and $j_{0.1}$, while the integrals from 0.1 to higher concentrations were determined graphically. The results are given in Table II.

TABLE II

m	θ	$0.4343\ j$	$0.4343\int_0^{0.1}\frac{j}{m}\,dm$	$0.4343\int_{0.1}^{m}\frac{j}{m}\,dm$	$0.00268\int_0^{m}\frac{\theta}{m}\,d\theta$	γ'
0.001						0.959
.005						.914
.01	0.010					.884
.05	.048					.785
.1	.094	0.0356	0.1005		0.0002	.731
.2	.186	.0413		0.0269	.0005	.677
.5	.459	.0458		.0673	.0012	.610
1	.917	.0454		.0991	.0023	.566
1.5	1.398	.0404		.1167	.0035	.548
2	1.894	.0331		.1274	.0047	.542
2.5	2.410	.0256		.1340	.0061	.542
3	2.949	.0174		.1379	.0074	.545
3.5	3.506	.0100		.1400	.0089	.550
4	4.063	.0035		.1409	.0104	.555
4.5	4.635	− .0026		.1410	.0120	.561
5	5.215	− .0078		.1405	.0136	.566
5.5	5.805	− .0130		.1395	.0153	.572
6	6.408	− .0180		.1382	.0170	.578
6.5	7.011	− .0228		.1365	.0188	.585
7	7.624	− .0274		.1347	.0205	.591
7.5	8.260	− .0319		.1326	.0223	.598
7.8	8.622	− .0343		.1313	.0234	.601

Up to 4 molal solution, there are available sufficient data to correct the values of γ' to 100°. Rossini[23] gives values of $\bar{L}_1$ at 18° up to $m = 2.0$. Using the heat capacity data of Randall and Rossini[24] we have calculated these values to 25°. The values of $\bar{L}_1$ given by Wüst and Lange[25] have been used from two to four molal. Randall and Rossini[24,26] give values of $\bar{C}_{p_1}$ up to $m = 2.5$. Up to this molality, they have shown that $\bar{C}_{p_2}$ and Φ, the apparent molal heat capacity of the solute, are both substantially

[23] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

[24] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[25] Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

[26] Up to $m = 2.0$ the heat capacity data for aqueous solutions of potassium chloride have been summarized by Rossini [Rossini, *Bur. Standards J. Research*, **7**, 47 (1931)]. He gives an equation for $(\bar{C}_{p_1} - \bar{C}^{\circ}_{p_1})$ which results in slightly different values for this difference than those we have used. No change in γ would result from their use.

linear functions of $\sqrt{m}$. We have therefore extrapolated their results to 4 molal. Since the resultant values of $\bar{C}_{p_2}$ so obtained are in fairly good agreement with those calculated from the specific heat data in the "International Critical Tables,"[27] they are sufficiently accurate for our present

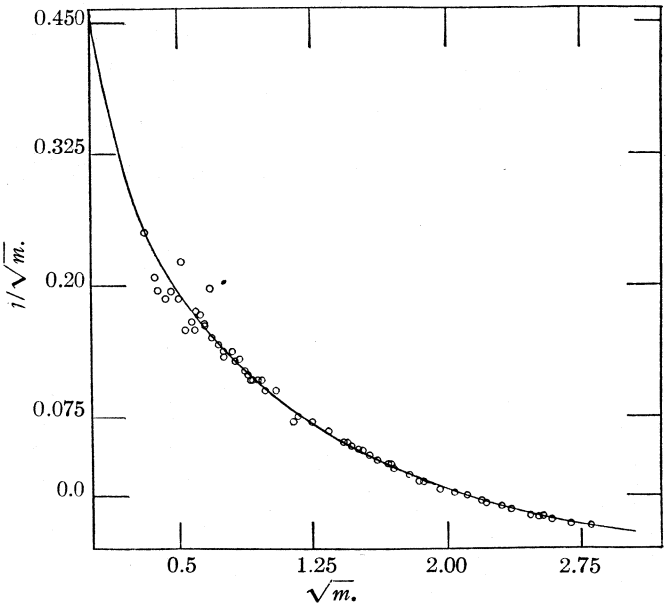


Fig. 3.

purpose. $\bar{C}_{p_1}$ was then calculated from $\bar{C}_{p_2}$, Φ, and $\bar{C}^{\circ}_{p1}$. The data used and the results obtained are given in Table III.

TABLE III

m	$\bar{L}_{1(298.1)}$	$(\bar{C}_{p1} - \bar{C}^{\circ}_{p1})_{(298.1)}$	$\gamma_{298.1}$
0.2	0.02	−0.009	0.677
.5	.76	− .033	.610
1	2.88	− .099	.566
1.5	5.85	− .187	.549
2	9.81	− .310	.544
2.5	14.6	− .410	.544
3	19.0	− .532	.548
3.5	23.2	− .664	.553
4	27.1	− .805	.559

Up to 2 molal, we have the necessary data for calculating the activity coefficients at 100° from those at 25° as given by Harned.[28] The values of $\bar{L}_2$ were calculated to 25° from those at 18° as compiled by Rossini.[23] The heat capacity data are from Randall and Rossini.[24,26] Table IV gives

[27] "International Critical Tables," Vol. V, p. 115.

[28] Harned, THIS JOURNAL, **51**, 416 (1929).

the data used and the results, together with our observed values for comparison. The agreement is satisfactory.

TABLE IV

m	$\bar{L}_{2(298.1)}$	$(\bar{C}_{p2} - \bar{C}^{\circ}_{p2})_{(298.1)}$	$\gamma_{298.1}$	$\gamma_{373.1}$ (calcd.)	$\gamma_{373.1}$ (obs.)
0.001	24	0.47	0.965	0.959	0.959
.005	54	1.06	.926	.912	.914
.01	60	1.50	.899	.882	.884
.05	87	3.35	.815	.787	.785
.1	95	4.75	.764	.731	.731
.2	70	6.80	.712	.676	.677
.5	− 58	10.95	.644	.610	.610
1	−195	15.85	.597	.562	.566
1.5	−327	19.75	.576	.542	.549
2	−448	23.15	.569	.536	.544

Finally, we have evaluated the constants A and B in the equation of Hückel, using 55.3 as the dielectric constant. The densities used are those given in the "International Critical Tables."[29] Up to 4 molal the activity coefficients at 100° can be represented satisfactorily by the equation

$$\log \gamma = \frac{-0.612\sqrt{c}}{1 + 1.19\sqrt{c}} + 0.046\, c - \log (1 + 0.036\, m)$$

The comparison of the observed results with those calculated from the equation are given in Table V.

Although density data are given only up to about 5 molal, we have extrapolated up to our highest concentration and give the calculated values of γ in comparison with the measured values of γ' which will not differ greatly from γ, even at these high concentrations. It is apparent that the equation is satisfactory through the entire concentration range. Since correction to 100° raises the values of γ', it is probable that the agreement in the concentrated solutions would be improved if such a correction could be made.

TABLE V

m	0.001	0.005	0.01	0.05	0.1	0.2	0.5	
γ (calcd.)	.959	.914	.884	.786	.732	.676	.606	
γ (obs.)	.959	.914	.884	.785	.731	.677	.610	
m	1.0	1.5	2.0	2.5	3.0	3.5	4.0	
γ (calcd.)	0.566	0.551	0.545	0.545	0.547	0.551	0.556	
γ (obs.)	.566	.549	.544	.544	.548	.553	.559	
m	4.5	5.0	5.5	6.0	6.5	7.0	7.5	7.8
γ (calcd.)	0.562	0.569	0.576	0.583	0.590	0.598	0.606	0.610
γ' (obs.)	.561	.566	.572	.578	.585	.591	.598	.601

From the value of A and the dielectric constant, the parameter, a, representing the distance of closest approach of the ions, becomes 3.40 Å., as

[29] "International Critical Tables," Vol. III, p. 87.

compared with 3.28 Å. calculated from Harned's constant at 25°. This increase would seem to confirm the results of Harned and Nims,[30] whose data on sodium chloride show that a increases from 3.60 Å. at 25° to 3.78 Å. at 40°. On the other hand, if our value of A is lowered to 1.15, the values of a would be the same at the two temperatures. Such a value of A with an increase in B to 0.049 gives an equation which reproduces our measured values up to 4 molal nearly as well as the one used, but gives larger deviations at the higher concentrations, unless the correction of the activity coefficient to 100° is larger than we think it to be. Thus, our results up to 4 molal may also be said to agree with the findings of Cowperthwaite and La Mer,[31] who found a to remain constant from 0 to 37.5° for dilute solutions of zinc sulfate. Our results, therefore, offer no conclusive evidence on the effect of temperature on a. The constant B has increased with temperature. From the work of Butler[32] it follows that if we assume the lowering of the dielectric constant of the solvent and the ionic radii of the solute to be independent of temperature, the constant B should be inversely proportional to the temperature and the square of the dielectric constant. Using Harned's value of $B = 0.034$ and our own result, the ratio $B_{100°}/B_{25°}$ is 1.35, while the ratio calculated from Butler's relation and Wyman's values of the dielectric constants is 1.61.

Summary

Two new apparatus for measuring the elevation of the boiling point at constant pressure have been described.

The elevations for potassium chloride in water have been measured up to 7.8 molal solution. From the results, the activity coefficients of the solute have been calculated. Up to 4 molal, these coefficients have been corrected to 100°, and up to 2 molal they have been compared with those calculated from 25°. The constants of the equation of Hückel have been evaluated. The equation is satisfactory through the entire concentration range.

NEW HAVEN, CONNECTICUT

[30] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

[31] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[32] Butler, *J. Phys. Chem.*, **33**, 1015 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OREGON]

THE STRUCTURE OF CELLULOSE ACETATE GELS FROM STUDIES OF DIFFUSION

BY KARL KLEMM AND LEO FRIEDMAN

RECEIVED FEBRUARY 26, 1932 PUBLISHED JULY 6, 1932

The structure of gels of gelatin and agar-agar has been the subject of earlier investigation by one of the authors.[1] This paper is a report of studies made on the gel system cellulose acetate in benzyl alcohol, which was chosen for study in order that the structural investigations might be carried out in the absence of water. By this means the possibility of structural modification resulting from the presence of ions and from contamination of the gels by molds was avoided. As a further precaution against changes of the original structure during the investigations, methyl and ethyl alcohol were selected as diffusates because of their negligible degrees of ionization in benzyl alcohol and the fact that cellulose acetate is insoluble in either.

Method and Materials.—The method of studying diffusion employed in this work was that developed by Friedman and Kraemer,[1] for their study of gelatin and agar-agar systems. In this method, a mass of material, the diffusate, is dissolved in a given mass of the dispersing medium of the gel. A volume of this solution just equal to the volume of the gel to be studied is placed upon the gel and kept stirred. The diffusate penetrates into the gel, the extent of diffusion as a function of time being determined at appropriate intervals.

The equation connecting the diffusion coefficient with the time–concentration data in the liquid layer was developed for this particular method by March and Weaver.[2] In its expanded form, it becomes

$$V = 1/2 - [0.327e^{-4.117T} + 0.0766e^{-24.14T} + 0.0306e^{-63.68T} + 0.0160e^{-123T} + \ldots\ldots] \quad (1)$$

V is the fraction of the material that has diffused into the gel at a given time. $T = Dt/a^2$, where D is the coefficient of diffusion, t is the time in seconds, and a is the height of the gel layer and also that of the liquid layer.

By substituting values for T, it was possible to plot a theoretical curve. To determine the value of the diffusion coefficient, D, for a given system, the value of T corresponding to the experimentally determined value of V is read from the theoretical curve. Then the value of D is calculated from the equation $D = a^2T/t$.

The cellulose acetate used was a chemically pure product obtained from the Eastman Kodak Company and received no treatment beyond

[1] Friedman and Kraemer, THIS JOURNAL, **52**, 1295 (1930).

[2] March and Weaver, *Phys. Rev.*, **31**, 1072 (1928).

sufficient mixing to ensure its homogeneity. Cellulose acetate, although insoluble in water, is of a porous nature, and it was found necessary to remove the adsorbed moisture in an electric oven at 92°. The loss amounted to from 2 to 2.5% by weight. Since water is only very slightly soluble in benzyl alcohol, no drying of the chemically pure solvent, benzyl alcohol, also obtained from the Eastman Kodak Company, was attempted.

Experimental Procedure

Sols of various concentrations were prepared by heating the proper mixtures of cellulose acetate and benzyl alcohol for one hundred fourteen minutes at 100°. The sols were permitted to gel in a thermostat at 25° and after thirty-six hours, a time interval sufficient to ensure complete gelation, a diffusate solution was placed upon the respective gels and the diffusion studies were started. The changes in concentration of the diffusate were measured by tracing the refractive index changes of the solution and the calculation of the diffusion coefficients made as described above. An example of the results obtained is shown in Table I.

TABLE I

DIFFUSION OF METHYL ALCOHOL INTO A CELLULOSE ACETATE GEL

3% methyl alcohol solution. 15% cellulose acetate. Area of bottle, 20.83 sq. cm. Total shift, 23.57.

Time in minutes	Refractometer shift	V	T	$D \times 10^5$
1399	2.41	0.1023	0.00965	0.2376
1545	2.52	.1081	.01092	.2434
1700	2.62	.1112	.01166	.2367
2037	2.81	.1192	.01360	.2299
2744	3.23	.1371	.01870	.2347
2872	3.31	.1405	.01971	.2364
3043	3.40	.1443	.02080	.2354
3152	3.46	.1468	.02170	.2371
3251	3.56	.1510	.02300	.2436
3434	3.64	.1544	.02420	.2427
4296	3.87	.1642	.02810	.2254
				Average 0.2366

Effect of Concentration of Gel on Rate of Diffusion.—To show the effect of concentration of cellulose acetate upon the gel systems studied, determinations of the rates of diffusion were made upon gels of concentrations ranging from 2 to 20% cellulose acetate by weight. The numerical results obtained are shown in Table II and are plotted in Fig. 1.

The diffusate in Runs I, II, and III was C_2H_5OH from a 10% solution; in Run IV from a 3% solution; in Run V, CH_3OH from a 3% solution.

A study of the curves (Fig. 1) reveals that the diffusion coefficient is a linear function of the cellulose acetate concentration. The values of the coefficients for the various runs indicate the impossibility of reproducing a

TABLE II

DIFFUSION COEFFICIENTS × 10^5 *versus* CONCENTRATION OF GELS

Concn. of gel, %	Run No. I	II	III	IV	V
20	0.0635		0.1081		
17.5					0.0719
15		0.1016		0.1158	
12		.1368		.1369	.1482
10	.1279		.2337		
9		.1550		.1738	
7.5	.1481		.2866		.1854
6		.1957		.2029	.1958
5	.1680		.3134		
4		.2273		.2377	
2.5	.2024		.3686		.2484

given system with exactitude. This may be attributed either to the inevitable slight differences in the thermal treatment of the gels of one run from that of another or to the impossibility of even a statistical control of the incomplete or imperfect crystallization that results in gel formation.

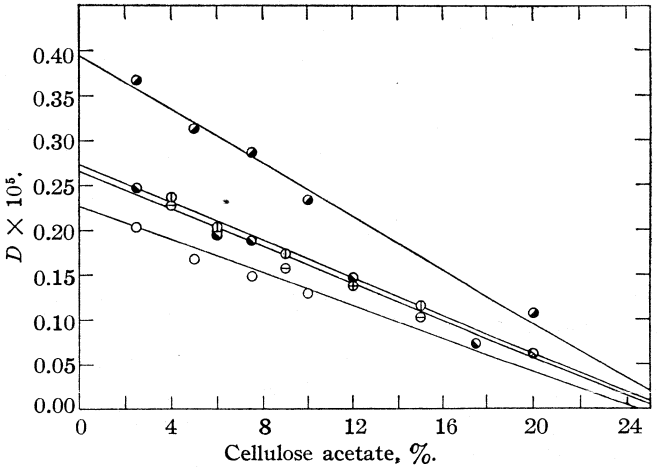


Fig. 1.—Diffusion in cellulose acetate gels: ○, Run no. I; ⊖, Run no. II; ◑, Run no. III; ⓘ, Run no. IV; ◐, Run no. V.

Determination of the Effective Pore Radii.—In the determination of the effective average pore radius of a given gel the formula derived by Friedman and Kraemer was used,[1] which for these determinations takes the form

$$D_{alc.} = D_{gel} \cdot (1 + \alpha) \cdot (1 + \pi) \cdot (1 + 2.4r/R) \qquad (2)$$

$D_{alc.}$ is the diffusion coefficient of the diffusate in benzyl alcohol. D_{gel} is the diffusion coefficient of the diffusate in a given gel system at the same concentration of diffusate employed in determining $D_{alc.}$. α is the correc-

tion factor for the viscosity and is equal to the quotient of $D_{alc.}$ divided by D_{gel} extrapolated to zero concentration of cellulose acetate. π is the correction for mechanical blocking and is calculated from Dumanski's formula:[3] $\pi = \sqrt[3]{(g/d)^2}$ where g is the number of grams of cellulose acetate in 1 cc. of gel, and d is the density of the cellulose acetate. $(1 + 2.4r/R)$ is an approximation for the determination of the average pore size. It was taken from Ladenburg's correction for the fall of bodies in capillary tubes and was originally intended to be applied to Stoke's Law. r is the radius of the diffusate molecule and R is the effective average radius of the pores in the gel.

The values of the diffusion coefficients for methyl and ethyl alcohol in benzyl alcohol at 25° and in the concentrations used in the experiments were not extant and were determined by the method devised by Northrop,[4] and perfected and standardized by McBain and Liu.[5]

This method depends upon the separation, by means of an indifferent membrane with pores of microscopic size, of two homogeneous bodies of solution. In this way the diffusion gradient is confined within this membrane. The results obtained are relative but are standardized by the measurement of a single standard solution the absolute value of whose diffusion coefficient is known at some definite concentration and temperature.

The equation relating the diffusion coefficient of a given system to the time during which diffusion occurs was derived from Fick's equation, $ds = DA(dc/dx)dt$, and takes the form

$$KD = \frac{\log C_0 - \log (C_0 - 2C)}{t} \qquad (3)$$

K is the cell constant. C_0 is the original concentration of the diffusate within the cell used. C is the concentration of diffusate outside the cell at a given time. D is the diffusion coefficient of the diffusate at the concentration and temperature of the experiment. t is the time elapsed between the beginning and end of the diffusion. The values so obtained are shown in Table III.

TABLE III

DIFFUSION COEFFICIENTS OF CH_3OH AND C_2H_5OH IN BENZYL ALCOHOL AT 25°

Diffusate	CH_3OH	C_2H_5OH	C_2H_5OH
Concn. (% by weight)	3	3	10
$D \times 10^5$	0.8144	0.8080	0.5463

By substitution of the values in Table III into equation (2) the values given in Table IV were obtained.

[3] Dumanski, *Kolloid-Z.*, **3**, 210 (1908).

[4] Northrop and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

[5] McBain and Liu, THIS JOURNAL, **53**, 58 (1931).

TABLE IV

EFFECTIVE PORE RADII IN mμ IN GELS OF DIFFERENT CONCENTRATIONS

Run no.	Concentration of gel as percentage cellulose acetate 2%	5%	10%	15%	20%
I	17.451	5.928	1.621	0.638	0.213
II	18.195	5.996	1.732	.711	.263
III	19.894	6.186	1.883	.792	.306
IV	17.497	5.882	1.795	.747	.291
V	17.918	5.551	1.553	.633	.234
Mean	18.191	5.909	1.717	0.704	0.261
Max. dev.	9%	6%	10%	12½%	18%

Discussion of Results

By plotting the pore radii as ordinates against the concentrations as abscissas (Fig. 2), the pore radii are seen to approach 18 mμ at 2% concentration of cellulose acetate and 0 mμ at 23% gel. However, the pore openings would be expected to become discontinuous at a concentration below 23%, providing the preparation of a homogeneous gel of such concentration were not beyond experimental realization.

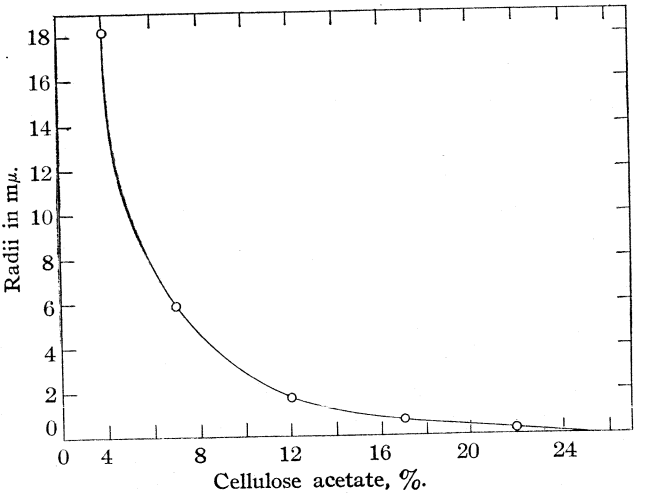


Fig. 2.—Change of pore radii with concentration.

The employment of the theoretical diffusion curve developed by March and Weaver[2] for the work of Friedman and Kraemer[1] gives a constant diffusion coefficient at any time interval for a given gel, even in such diverse systems as gelatin in water, agar-agar in water, and cellulose acetate in benzyl alcohol. This strongly supports the validity of the diffusion equation employed in the investigation and the values of the coefficients obtained.

It is considered that the above results, if not conclusive proof of the liquid–solid theory of gel structure, are at least very strong evidence in favor of the theory.

That the rate of diffusion decreases with increased gel concentration is in support of the pore theory, since the effective pore radii would be expected to decrease with increased concentration of the dispersed medium until the pores should become discontinuous.

The high values of the determined diffusion coefficients are inconsistent with those to be expected in a solid solution where, as a result of the enormous increase of the viscosity of the system upon gelation, diffusion should practically cease.

The change in magnitude of the pore radii with change in the concentration of cellulose acetate is seen from Fig. 2 to be an exponential function. This is in accord with the liquid–solid theory, which infers a change of effective pore radius with change in concentration. Any change in effective pore radius must be followed by a change in the number of pores within a given volume of gel. Since gel formation is conceded to be an incomplete precipitation of the dispersed medium, the resulting pore openings might be considered as consisting of minute tubes of varying lengths, chaotically arranged, but each intersecting others to form continuous open passages completely through a gel. The thickness of the pore walls is also undoubtedly a function of the concentration. That the radii and the number of the pore openings change with concentration has been demonstrated by this investigation. The fact that approximate equations for the experimentally determined curve, Fig. 2, obtained by the method of least squares lead to curves more nearly symmetrical with the experimental curve as the number of terms (and consequently the degree of the function) increases, supports the postulates mentioned above.

Summary

1. A study of the structure of gels of cellulose acetate in benzyl alcohol has been made by measuring diffusion into the gels with time.

2. It has been shown that the diffusion law holds for the penetration of the employed diffusates into cellulose acetate gels.

3. The validity of the diffusion equation employed in the investigation has been supported by the diffusion coefficients obtained.

4. The values of the effective pore radii of gels of various concentrations have been determined and found to be of the same order of magnitude as those obtained by Friedman and Kraemer for gelatin and agar-agar systems.

5. The high values of the experimentally determined diffusion coefficients render untenable the solid solution theory of gels.

6. The change in pore radii with change in concentration has been shown to be an exponential function, a rate of change to be expected in the liquid–solid theory.

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CONSTITUTION OF CERTAIN COBALTAMMINE BASES

BY ARTHUR B. LAMB AND ROGER G. STEVENS

RECEIVED FEBRUARY 27, 1932 PUBLISHED JULY 6, 1932

In contrast with the simple hydroxides of cobalt many of the complex bases of cobalt are easily soluble and relatively strong. Triethylenediamine cobaltic hydroxide $[Co(C_2H_4(NH_2)_2)_3](OH)_3$, for instance, is a very soluble, deliquescent substance which displaces both silver oxide and ammonia from their respective salts and whose solution is caustic, absorbing carbon dioxide from the air.

The conductivities of some nine of these cobaltammine bases were measured some time ago,[1] and it was found, in agreement with the above behavior, that these bases are highly ionized. Thus in 0.00133 molar solution at 0° triethylenediamine cobaltic hydroxide appeared to be 88.6%, while the univalent base, 1,6-dinitro-tetrammine hydroxide, 1,6-$[Co(NH_3)_4(NO_2)_2]OH$, appeared to be 95% ionized.

These measurements disclosed a further important regularity. When water molecules were present within the complex of the bromide from which the bases were prepared, the ionization of the bases was decidedly less than when they were absent. Thus in solutions of the above concentration, one such molecule of water in the complex lowered the percentage ionization of the base by about 30%, two molecules by about 60%. The assumption was then made that every molecule of water in the complex cation was replaced by an hydroxyl group as soon as the free base was formed. In other words, for every molecule of water in the complex, one hydroxyl ion was eliminated from the outer sphere. Percentage ionizations were calculated on this basis and were very large, but in no case did they exceed 100%.

Werner[2] long before had assumed the existence of such hydroxo or "anhydro" bases as he called them. Job[3] from observations of the change in conductivity of solutions of aquo-pentammine cobaltic sulfate upon the addition to it of solutions of baryta showed that in this case the first hydroxyl group liberated by the precipitation of barium sulfate became complexly bound, apparently replacing the single water molecule in the complex. The two additional hydroxyl groups liberated remained in an ionized condition. Job made similar observations with diaquo-tetrammine cobaltic sulfate, but in this case, while evidently considering that the two water molecules in the complex were also replaced by the first two hydroxyl

[1] Lamb and Yngve, THIS JOURNAL, **43**, 2352 (1921).

[2] Werner, "Neuere Anschauungen," Braunschweig, 1913, pp. 264–268.

[3] Job, "Recherches sur Quelques Cobaltammines," Paris and Lyon (1921); *Compt. rend.*, **174**, 615 (1922).

ions liberated, Job concluded that the resultant ion $[Co(NH_3)_4(OH)_2]^+$ was unstable and underwent polymerization of some kind.[4]

In this situation it appeared to us desirable to ascertain more definitely whether such a replacement of complexly bound water molecules by hydroxyl ions does in general take place and, if so, to what extent. To this end we have prepared solutions of some five cobaltammine bases by the action of silver oxide on cobaltammine bromides, containing either 0, 1 or 2 molecules of water in the complex cation, and have titrated them with a relatively concentrated solution of hydrochloric acid by means of conductivity measurements. From the changes in conductivity thus observed it has been possible to infer, as did Job in an analogous case, whether the hydroxyl groups originally present are ionized or un-ionized. Moreover, it has also been possible, from the numerical values of the conductivity at the breaks in the titration curves corresponding to the exact neutralization of one or more hydroxyl groups, to check the correctness of the above inferences, since the conductivities of the corresponding substances are either known or can be computed with reasonable accuracy.

Experimental

Preparation of Materials.—The hexammine and the carbonato tetrammine cobaltic bromides were the same materials as had previously been used by Lamb and Yngve.[1] The aquo-pentammine and diaquo-tetrammine cobaltic bromides were prepared by the methods of Jörgensen;[5] the aquo-pentammine chromic bromide by the method of Christensen.[6] The specific conductivity of the water used varied between 0.8 and 1.5 $\times$ 10^{-6} mhos. The solutions prepared from these were all 0.004 molar.

Apparatus.—The conductivity cell consisted of dip-electrodes of platinized platinum held at a fixed position in a closed 200-cc. Pyrex glass test-tube which was almost wholly submerged in an ice-bath (or in a water thermostat maintained at 25.00 $\pm$ 0.02°). A thermometer legible to 0.01° was placed in the solution itself. The Wheatstone bridge was of the usual spirally-wound type. The uncertainty of the minimum was always less than would correspond to an error of $\pm$0.1% in the conductivity. The cell was standardized against a 0.02 *M* solution of potassium chloride, the specific conductivity of this solution being taken as 0.002768 mhos at 25.00°. The standardization was repeated frequently in the course of the measurements and no variations greater than $\pm$0.1% were observed.

Procedure.—It was necessary not only to guard the solutions of the free bases from contact with the air but also both to prepare and to measure them expeditiously since they undergo a slow decomposition even at 0°, particularly in contact with platinum electrodes. A procedure was therefore adopted to meet these requirements as follows.

A pestle and a small mortar containing a slight excess of moist silver oxide were cooled to 0°. A weighed quantity of ammine bromide sufficient to give a 0.004 *M* solution was then added to the silver oxide and triturated for one minute, and the solution rapidly filtered by suction into a 100-cc. delivery volumetric flask packed in ice. The

[4] Ref. 2, pp. 49–54.

[5] Jörgensen, *Z. anorg. Chem.*, **2**, 294 (1892); *J. prakt. Chem.*, [2] **31**, 62 (1885).

[6] Christensen, *ibid.*, [2] **23**, 27 (1881).

mortar was then washed out several times, and the residue on the filter ten times, with ice-cold conductivity water. The solution was brought up to the mark with more of this water, thoroughly mixed, and poured into the dry cell immersed in an ice-bath. The solution was then rapidly stirred by a guarded movement of the dip-electrodes, since a too violent up and down movement was found to introduce a noticeable amount of carbon dioxide. All of these operations were conducted with the greatest possible dispatch. They usually required between six and ten minutes, counting as zero time the moment when the ammine bromide was added to the silver oxide. The temperature of the solution at this point was usually about +1° and several minutes longer was usually required for the temperature to reach substantially 0° when conductivity measurements were begun and continued at frequent intervals. Ice-cold 0.02 *M* hydrochloric acid was then added in 5-cc. portions (corresponding to one quarter of a molecule of acid per molecule of ammine); a minute was allowed for readjustment of the temperature, when stirring was resumed and conductivity measurements were again made.

The Water Correction.—Since the conductivity of ordinary carefully distilled water is chiefly due to the carbon dioxide present, and since this will neutralize two equivalents of hydroxyl ion in alkaline solution, thus replacing a rapid ion by a slow one ($CO_3^=$), the conductivity of a dilute solution of a base in such water will appear slightly too low. The correction for an isolated solution at 0° is equal to $8.3 \times 10^6 \times L^2_{H_2O}$, where L_{H_2O} is the conductivity of the water; or taking[7] $L_{H_2O} = 1 \times 10^{-6}$ mhos, the correction is -8.3×10^{-6} mhos. This has been applied to the specific conductivities up to but not beyond the point of neutralization (minimum conductivity).

Results.—The results of a single representative experiment, namely, that with aquo-pentammine cobaltic hydroxide, are given in full in tabular form (Table I) to illustrate the procedure. The experimental results as a whole are shown in graphical form in Fig. 1.

TABLE I

TITRATION OF AQUO-PENTAMMINE COBALTIC HYDROXIDE (0.004 *M*) WITH HYDROCHLORIC ACID (0.02 *M*)

Temp., 0.0°

Time, minutes	HCl added, equiv.	Specific conductivity, 1/ohm		Molecular conductivity, 1/ohm
		Observed	Corrected	
15	..	1034.2	1042.5	260.5
16	..	1032.5	1040.5	260.1
19	..	1025.0	1033.0	258.2
26	..	1016.6	1024.6	256.1
27	0.25	....	....	...
28	..	903.9	911.9	239.4
29	..	902.5	910.5	239.0
30	0.50	....	....	...
31	..	794.9	802.9	220.8
33	0.75	....	....	...
34	..	691.8	699.8	201.2
36	1.00	....	....	...
37	..	599.3	607.3	182.2

[7] Ref. 1, p. 2354.

TABLE I (*Concluded*)

Time, minutes	HCl added, equiv.	Specific conductivity, 1/ohm		Molecular conductivity, 1/ohm
		Observed	Corrected	
39	1.25	....	....	...
40	..	514.6	522.6	163.3
41	..	512.5	520.5	162.6
42	1.50	....	....	...
43	..	437.5	445.5	144.8
45	1.75	....	....	...
46	..	380.7	388.7	131.2
47.5	1.80	....	....	...
48	..	378.4	386.4	131.4
48.5	1.85	....	....	...
49	..	379.8	387.8	132.8
49.5	1.90	....	....	...
50	..	389.1	389.1	134.2
50.5	1.95	....	....	...
51	..	399.2	399.2	138.7
51.5	2.00	....	....	...
52	..	407.9	407.9	142.8
55	2.25	....	....	...
56	..	452.1	452.1	163.9
58	2.50	....	....	...
59	..	487.1	487.1	182.6
65	2.75	....	....	...
66	..	526.0	526.0	203.8
72	3.00	....	....	...
89	..	574.3	574.3	229.7
90	3.25	....	....	...
93	..	705.7	705.7	291.1
102	3.50	....	....	...
103	..	840.8	840.8	357.3
105	3.75	....	....	...
106	..	961.0	961.0	420.4
108	4.00	....	....	...
109	..	1073.0	1073.0	482.8

As can be seen from the table, the initial conductivities show a slow progressive decrease even after the temperature has become constant. The decrease was more rapid when the solution was not stirred. This indicates a slow decomposition accelerated in the presence of the platinized electrodes. This is in agreement with earlier observations.[8]

The adjustment of the neutralization equilibrium was instantaneous so far as our measurements could disclose, although after the addition of the first portions of acid there was a slight progressive decrease which was evidently caused by the incomplete removal of the heat of neutralization. This instantaneous adjustment of the neutralization equilibrium is what

[8] Ref. 1, p. 2354. Also Lamb and Larson, THIS JOURNAL, **42**, 2025 (1920); and others.

would be expected when free hydroxyl and hydrogen ions interact. It is of great interest that the adjustment should also be instantaneous when all the free hydroxyl ions have been removed and only the complexly bound hydroxyl groups are involved. This indicates either that the equilibrium between hydroxo ion and water on the one hand and aquo ion and hydroxyl

$$[Co(NH_3)_5OH]^{++} + H_2O \rightleftharpoons [Co(NH_3)_5H_2O]^{+++} + OH^-$$

ion on the other is instantaneously adjusted, or that the equilibrium involving the direct combination of hydroxo ion with hydrogen ion, as postulated by Werner,[2] is instantaneously adjusted.

$$[Co(NH_3)_5OH]^{++} + H^+ \rightleftharpoons [Co(NH_3)_5H_2O]^{+++}$$

An examination of Fig. 1 leads to the following deductions relative to the constitution of the several hydroxides.

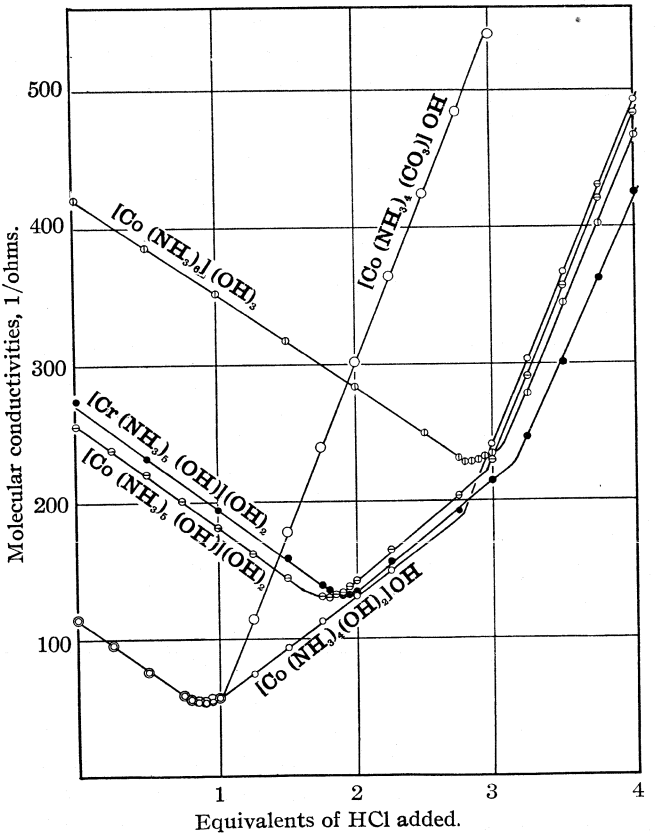


Fig. 1.—Titration of ammine bases by measurements of conductivity.

(a) Hexammine hydroxide, containing no complexly bound water, gives a curve with a uniform downward slope which reaches a minimum

at the point corresponding to an addition of three molecules of hydrochloric acid, and rises sharply thereafter. This is a normal curve such as would be expected for a highly ionized trivalent base.

(b) Pentammine hydroxide gives a curve which starts at a much lower point, indicating a much smaller concentration of hydroxyl ions. It slopes downward nearly parallel to the hexammine curve, but reaches a minimum after the addition of two molecules of acid.

Thereafter the curve rises moderately until another molecule of acid has been added, when it rises more steeply almost in superposition with the hexammine curve.

The part of the curve sloping downward evidently corresponds to the normal behavior shown by the hexammine curve; it records the replacement of fast hydroxyl ions by relatively slow chloride ions with a consequent decrease in conductivity. The next part of the curve, sloping moderately upward, is what would be expected if one un-ionized hydroxyl and one equivalent of added hydrogen ion were eliminated as water with the consequent introduction of a chloride ion into the solution and the conversion of the divalent into the trivalent ammine cation. The remainder of the curve, after the addition of the three molecules of acid, merely records the effect of adding relatively concentrated acid.

This curve, therefore, indicates that in pentammine cobaltic hydroxide one of the hydroxyl groups is complexly held, or but slightly ionized, while the other two are highly ionized at these concentrations.

(c) Tetrammine hydroxide gives a curve which shows the same phenomena as did the pentammine, but to a more pronounced degree. Here there is evidently a single, highly ionized hydroxyl group and two hydroxyl groups that are at most slightly ionized.

(d) Pentammine chromic hydroxide gives a curve corresponding very closely with that of the analogous pentammine cobaltic hydroxide.

(e) Carbonato-tetrammine hydroxide gives a curve that coincides almost exactly with the curve of the dihydroxo-tetrammine hydroxide down to the minimum of conductivity. This shows that it, too, has a single, highly ionized hydroxyl group, and that the two univalent cations have almost exactly the same mobilities. After the minimum, the carbonato curve diverges rapidly upward from the tetrammine curve, running nearly parallel to the curve for the addition of excess acid. It is evident that after the neutralization of the hydroxyl ion only a small fraction of the hydrogen ions combines with the carbonato radical during the time occupied by this measurement; otherwise, the rise in the conductivity would be much less rapid.

It is clear from these curves that in every instance where the base has been derived from an ammine having one or two water molecules in the complex, a corresponding number of hydroxyl groups are complexly

held[9] or, in other words, the water molecules have been fully displaced by hydroxyl groups which are held firmly in the complex.

The correctness of this conclusion can be checked by a comparison of the conductivities indicated by the titration curves at the various minima and points of inflection with the directly measured conductivities of the substances there present. The data for such a comparison have been collected in Table II.

TABLE II

MOLAR CONDUCTIVITIES AT POINTS OF INFLECTION

Ammine hydroxide	Acid, moles added per mole	Chloride present	Concn. $\times 10^3$ molar	Directly measured	Conductivity molar 1/ohms Directly measured	From curves	Ref.
Hexa	3	Hexammine	2.5	Chloride	231	229	10
Penta	3	Pentammine	2.5	Nitrate	224	227	11
Tetra	3	Tetrammine	2.5	Bromide	221	220	12
Penta	2	Hydroxo-pentammine	2.857	Nitrate	135	132	11
Tetra	1	Dihydroxo-tetrammine	3.39	Dinitro chloride	56	54	10
Tetracarbonato	1	Carbonato-tetrammine	3.39	Chloride	57	55	13

The agreement between the conductivities as read from the curves and those computed from independent measurements is good and confirms the conclusion that the water molecules in the complex have been completely replaced by firmly held hydroxo groups.[14]

Apparent Percentage Ionization.—With the hydroxo structure of these hydroxides thus clearly established, it is of interest to consider more fully the significance of the values of the apparent ionizations as calculated

[9] It can be seen from the curves that the various minima are invariably displaced slightly to the left of the exact integral numbers of added molecules of acid. This is probably due to the above-mentioned slight decomposition of the free base into lower cobaltic or cobaltous ammines and free ammonia. The neutralization of the ammonia in the presence of the residual stronger bases would cause an increase rather than a decrease in conductivity and a consequent premature rise in the curve.

[10] Harkins, Hall and Roberts, THIS JOURNAL, **38**, 2656 (1916).

[11] King, *J. Chem. Soc.*, **127**, 2107 (1928).

[12] Werner and Miolati, *Z. physik. Chem.*, **12**, 42 (1893).

[13] From measurements to be published later in another connection.

[14] The firmness with which these hydroxyl groups are held can indeed be calculated in the case of the pentammine and the tetrammine bases from the very skilful and ingenious measurements of Brönsted and Volqvartz [*Z. physik. Chem.*, **134**, 133 (1928)] of the "acid dissociation" of aquo ions. Their constants for this dissociation divided into the dissociation constant of water should give the dissociation constants of the hydroxo bases:

$$K_{B_1} = \frac{C_{OH^-} \times C_{[Co(NH_3)_5H_2O]^{+++}}}{C_{[Co(NH_3)_5OH]^{++}} \times C_{H_2O}} \text{ and } K_{B_2} = \frac{C_{OH^-} \times C_{[CO(NH_3)_4(H_2O)_2]^{+++}}}{C_{[CO(NH_3)_4(H_2O)OH]^{++}} \times C_{H_2O}}$$

These are respectively 1×10^{-10} and 3×10^{-11} for the pentammine and tetrammine ions.

on the basis of this structure by Lamb and Yngve from their measurements. For this purpose we have recomputed the values of Lamb and Yngve, using more recent data for the mobilities of certain of the ions than were available at that time. The results are collected in Table III.

TABLE III

APPARENT IONIZATIONS OF THE COBALTAMMINE BASES

Temperature, 0°. Concn. = 0.001336 *M*

Ammine hydroxides	μ_0^c (cations) 1/ohm	μ_0 1/ohm	μ (observed) 1/ohm	α, %
$[Co(NH_3)_6](OH)_3$	167	521	431.1	83
$[Co(en)_3](OH)_3$	115	469	375.4	80
$[Co(NH_3)_5OH](OH)_2$	78	314	261.8	83
$[Cr(NH_3)_5OH](OH)_2$	78	314	275.6	[88]
$[Co(NH_3)_4(OH)_2](OH)$	18	136	115.0	84
$[Co(en)_2(OH)_2](OH)$	18	136	117	86
$[Co(NH_3)_4CO_3](OH)$	19	137	119	87
1,2$[Co(NH_3)_4(NO_2)_2](OH)$	18.1	136.1	100	74
1,6$[Co(NH_3)_4(NO_2)_2](OH)$	17.9	135.9	117	86
$[Co(NH_3)_3(H_2O)(NO_2)_2](OH)$ $\rightleftharpoons$ $[Co(NH_3)_3(NO_2)_2(OH)]$	18	136	50	37

The mobilities of the various ammine ions have been computed as follows: that of the hexammine from its chloride and nitrate;[15] that of the triethylenediamine from the data of Werner and Herty[16] on the chloride at 25°, converting to international ohms and using the factor 1.8 derived from their other measurements to convert to 0°; that of the hydroxo-pentammine from the data of King[11] on the hydroxo nitrate by first computing n (= 1.5) in the Storch–Bancroft equation and then plotting $(C\mu)^{n-1}$ against $1/\mu$; the carbonato-tetrammine from the data of Werner and Miolati[17] on the nitrate at 25° by extrapolation, taking n = 1.33 and then converting to ohms and to 0° by the above-mentioned factor; that of the dinitro-tetrammines from the chlorides and nitrates;[18] that of the chromic hydroxo-pentammine on the well-supported assumption that it would be the same as that of the corresponding cobalt ammine; that of the dihydroxo-tetrammine and the dinitro-aquo-tetrammine on the assumption that they would be the same as that of the dinitro-tetrammines.

The apparent percentage ionization of all of these bases, except the last one shown in this table, is strikingly high. Thus the ionization of the univalent bases is only a little less than that of the alkali bases, while that of the trivalent bases is about the same as that of a *salt* of the same type, lanthanum chloride, at the same concentration. This high apparent

[15] Ref. 1, p. 2360.

[16] Werner and Herty, *Z. physik. Chem.*, **38**, 337 (1901).

[17] Werner and Miolati, *ibid.*, **21**, 234 (1896).

[18] Ref. 1, p. 2362.

ionization doubtless indicates, on the basis of present views as to electrolytic solutions, a substantially complete true ionization.

A still more striking feature of these values is their marked similarity irrespective of the nature of the central atom, or of the number or nature of the groups surrounding this atom; and perhaps most surprising of all, irrespective of the number of electric charges on the cation.

Plausible explanations can be advanced for most of the above observations.

(1) The slight ionization of the hydroxyl groups inside the complex and the high apparent and the presumably complete actual ionization of the hydroxyl groups outside the complex may be explained as follows. Water molecules in these quite stable complex substances, though held with considerable firmness to the central atom by coördinate links, are much more readily displaced from the complex by various acido groups than are ammonia, diethyleneamine and various other molecules. It is not surprising, therefore, that they can be quite completely displaced by hydroxyl ions. These become attached by strong non-polar links and are but slightly ionized. When, however, all six coördinate positions are occupied by firmly held ammonia molecules or the like, or by firmly held acido groups, the hydroxyl ion cannot penetrate this protective shell, cannot form a non-polar link and, being held at some distance from the central atom, is almost completely ionized.

(2) The similarity in the ionization of the bases may be due to the similarity of the general exterior architecture of the cations of these bases, since they all have six exterior groups held by non-polar valences (six electron pairs) around small central atoms whose outer electron shells are presumably also quite similar.[19]

(3) The absence of any marked effect on the ionization of the differences in the number of electric charges on the cation might be due to the "chemical effect" of the acido groups as compared with that of the ammonia molecule. This effect, on the basis of ordinary experience in organic chemistry, would tend to decrease the ionization of the base when the accompanying valence change tended to increase it. However, the lack, as above mentioned, of any apparent difference between the effect of dinitro, dihydroxo and carbonato groups on the ionization when there are no changes in valence argues against this explanation. Another possibility is that the shell of coördinated groups so alters the electrostatic field about the central atom that the simple valence-squared function of the Debye–Hückel equation no longer obtains.

[19] P. Ray, Nineteenth Indian Science Congress, Bangalore, 1932, Section of Chemistry, President's Address, p. 33. It should also be noticed that the most marked contrast among the percentage ionizations shown in our Table III is between the two stereoisomeric dinitro-tetrammines.

One further and significant conclusion may be drawn from Table III. The last hydroxide there listed exhibits a conductivity corresponding to a 37% ionization. Yet according to the above generalization that hydroxyl ions replace water molecules in the complex ion completely, the aquo-dinitro-triammine hydroxide should be converted completely into hydroxo-dinitro-triammine, and since this does not ionize, its solution should exhibit zero conductivity. It is clear that in this case hydroxyl ions do not replace water molecules in the complex at all completely.

Certain hydroxo salts also afford exceptions, although less marked ones, to this generalization, for it has been long known that their solutions exhibit marked alkalinity; hydroxo-aquo-tetrammine cobaltic chloride,[20] for instance, is a case in point.

Expressed in terms of the above explanation, either the water molecule in aquo-dinitro-triammine hydroxide is more firmly held, or is replaced with greater difficulty by negatively charged hydroxyl ions, than are the water molecules in the other complex ions that we have studied, so that only a partial replacement occurs. Assuming that the aquo base once formed would show about the same apparent ionization as the other bases (83%), it would follow that about (0.37/0.83) × 100 or 45% of the compound is present in the solution in that form. That is,[21]

$$[Co(NH_3)_3(NO_2)_2OH] + H_2O \rightleftharpoons [Co(NH_3)_3(NO_2)_2H_2O]OH \overset{83\%}{\rightleftharpoons} [Co(NH_3)_3(NO_2)_2H_2O]^+ + OH^-$$

(45% →)

Irrespective of any mechanism one can, however, say that this base is a much stronger one than other exclusively hydroxo bases, its dissociation constant being of the order of 10^{-5} as contrasted with 10^{-10} for the hydroxo-pentammine ion.

This restriction of our generalization, however, clarifies rather than darkens the interpretation of these phenomena. It is evident that the hydroxyl ion reacts with these aquo cations quite as do other anions. It is known that many anions will replace water molecules in such complex ions reversibly. Some anions do so extensively, others but slightly; some rapidly, others slowly.[22] The hydroxyl ion is thus not unique in its behavior. It is perhaps outstanding as compared with other anions in that it displaces the complexly held water molecules in the aquo ions *both* extensively and *very* rapidly.

[20] Werner, *Ber.*, **40**, 4133 (1907).

[21] The *mechanism* of this equilibrium could be either the direct aquation here shown or the mechanism postulated by Werner [*Ber.*, **40**, 4133 (1907)] and Brönsted [*Rec. trav. chim.*, **42**, 718 (1923)], namely,

$$H_2O \rightleftharpoons OH^- + H^+$$
$$+$$
$$[Co(NH_3)_3(NO_2)_2OH] \rightleftharpoons [Co(NH_3)_3(NO_2)_2H_2O]^+$$

[22] Lamb and Marden, THIS JOURNAL, **33**, 1873 (1911); Pers, *Compt. rend.*, **153**, 673 (1911); Lamb and Fairhall, THIS JOURNAL, **45**, 378 (1923).

Summary

1. It has been shown by conductimetric titration of several nominally trivalent ammine bases prepared from aquo ammine bromides that the complexly held water molecules have in these instances been completely displaced by an equivalent number of the hydroxyl ions. The adjustment of these displacement equilibria is rapid and the hydroxo groups formed are firmly held.

2. The apparent ionizations of the hydroxyl groups remaining outside of the complex are high and are nearly identical in each of these cases, irrespective of the nature of the central atom, the coördinated groups and the valence of the cation.

3. The replacement of the complexly held water molecules is not, however, universally complete. Stated otherwise, the hydroxo group may in certain cases be largely replaced by a water molecule and thereafter ionized.

4. This interaction between these aquo ions and hydroxyl ions is comparable to that between aquo ions and anions in general, although the replacement of water molecules by the hydroxyl group is relatively extensive and the attainment of equilibrium is unusually rapid.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 12]

THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. V. LEAD BROMIDE IN SILVER BROMIDE

BY EDWARD J. SALSTROM

RECEIVED FEBRUARY 29, 1932 PUBLISHED JULY 6, 1932

The investigation described in this paper represents a continuation of a series of studies on the thermodynamics of fused salt solutions begun by Hildebrand and Ruhle.[1] The system lead bromide in silver bromide was chosen because the melting points of their solutions permitted a study extending over the entire range of their composition. Thus it was believed that the activities of both the solvent and solute could be determined.

Experimental Part

The lead bromide was prepared by precipitation from a solution of lead acetate with excess hydrobromic acid. The precipitate was repeatedly washed by decantation with a 3% solution of hydrobromic acid and finally dried at 150° for several days. Silver bromide was similarly prepared by precipitation from a silver nitrate solution. The bromine and hydrogen bromide were prepared as previously described in the lithium bromide–silver bromide study.[2]

---

[1] Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

[2] Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).

The cells, apparatus and procedure remained essentially unchanged.[2] In short, the method was as follows. Silver bromide and lead bromide were weighed out in the desired proportions. The salts were carefully melted together in a Pyrex tube, mixed by stirring and poured in the molten state into the Pyrex cell containers. The final traces of moisture, oxidation and hydrolysis products occasioned by filling and sealing the cell containers were swept out by bubbling through the melt a dry stream of hydrogen bromide gas for at least an hour and a half. Bromine gas generated by the electrolysis of fused lead bromide which had been similarly purified was then bubbled through the electrolyte over a treated graphite rod[3] which served as the positive electrode. The negative electrode was a pure silver wire inserted into a tube leading into the bottom of the cell. Molten tin served as a thermostat bath. Equilibrium was attained in a couple of hours but in practice the cell was allowed to run overnight. Readings were then taken at regular temperature intervals in both ascending and descending series, all of which were in complete agreement.

The results are given in Table I and plotted in Fig. 1. The e. m. f. values given are the observed results corrected to take into account a thermoelec-

TABLE I

E. M. F.'S OF THE CELLS: Ag(s), AgBr(l), $PbBr_2$(l), Br_2(g)

Temp., °C.	E. m. f. obs., volt
Cell A (N_1 = 1.00)	
442.3	0.8031
453.6	.8000
456.0	.7989
467.0	.7956
490.9	.7887
499.9	.7866
521.4	.7803
524.4	.7795
531.7	.7769
538.3	.7751
556.2	.7702
565.0	.7680
Cell B (N_1 = 0.80)	
437.6	0.8183
468.5	.8099
499.5	.8014
520.5	.7958
551.0	.7878
551.4	.7877
571.3	.7826
Cell C (N_1 = 0.70)	
429.1	0.8295
439.8	.8264
475.7	.8169
510.0	.8077
541.7	.7993
569.7	.7921
Cell D (N_1 = 0.60)	
429.0	0.8391
451.4	.8331
452.2	.8329
474.3	.8271
502.5	.8198
520.7	.8152
554.5	.8071
567.1	.8038
Cell E (N_1 = 0.50)	
428.5	0.8496
441.4	.8466
468.8	.8399
496.0	.8334
521.9	.8275
545.2	.8221
547.4	.8216
567.7	.8173
Cell F (N_1 = 0.40)	
423.6	0.8639
429.6	.8627
461.9	.8549
485.5	.8501
507.7	.8453
545.5	.8364
568.5	.8316
Cell G (N_1 = 0.30)	
438.0	0.8756
474.6	.8683
511.5	.8615
529.5	.8584
547.2	.8549
560.6	.8525
Cell H (N_1 = 0.20)	
427.0	0.9012
432.9	.9000
436.0	.8993
457.3	.8966
488.3	.8916
494.7	.8904
508.9	.8881
513.9	.8877
518.9	.8866
541.1	.8831
562.7	.8798
Cell I (N_1 = 0.10)	
430.7	0.9426
459.2	.9399
483.6	.9369
508.0	.9342
530.0	.9316

[3] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).

tric effect[3] caused by the fact that a definite temperature gradient exists in each electrode. Values for the cell containing pure silver bromide were those obtained in a previous lithium bromide-silver bromide investigation.[2]

The extreme deviation of the observed values from a straight line drawn through them in Fig. 1 is 0.5 millivolt and the mean deviation is less than 0.1 millivolt.

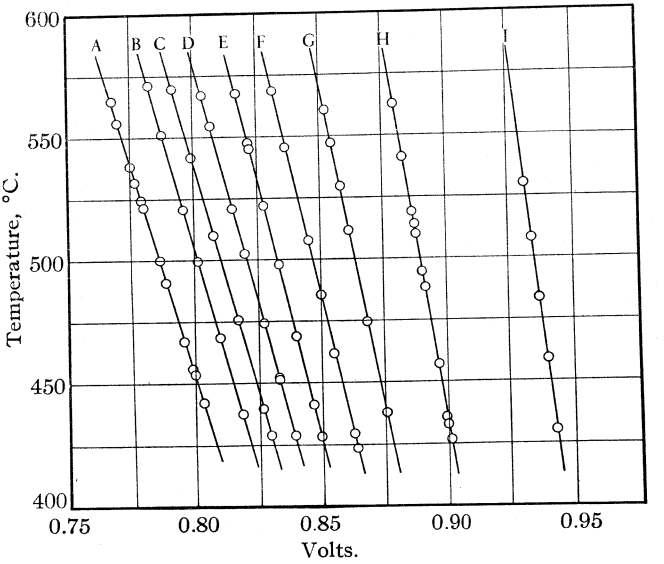


Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag, AgBr, $PbBr_2$, Br_2. See Table I for mole fractions of silver bromide.

To determine how the volume of a mole of solution varies with composition, density determinations were made upon a solution containing a half mole fraction of each salt. The method used consisted of weighing a tungsten-weighted quartz bulb, suspended by a very fine platinum wire, first in air, then in water and finally at various temperatures in the fused salt solution, correcting[4] each time for the expansion of quartz. The bulb was sharply tapped before each reading to remove any adhering bubbles of gas. The fused solution used in the density measurements was purified as in the case of the cells by bubbling dry hydrogen bromide gas through the melt for two hours.

The observed density values may be expressed by the equation, $d^t = 6.243 - 0.00146t$ and are given in Table II.

[4] A calculation of the effect of the buoyancy of air upon the bulb was made and it was found to be negligible. Data are not available for calculating the influence of surface tension of the fused solution upon the suspending wire but since its diameter was less than 0.1 mm. it is believed that such corrections would also prove to be negligible.

TABLE II

DENSITIES OF A 0.5 MOLE FRACTION OF LEAD BROMIDE IN SILVER BROMIDE

Temp., °C.	Density	Temp., °C.	Density
493.7	5.523	545.9	5.446
507.9	5.502	558.2	5.428
522.0	5.481	572.2	5.409
533.9	5.463	581.6	5.395

With the aid of density values for silver bromide obtained by Lorenz and Höchberg[5] and for lead bromide obtained by Lorenz, Frei and Jabs,[6] the molal volumes of silver bromide and lead bromide have been calculated at 500° to be 34.10 cc. and 66.53 cc., respectively. A half mole fraction solution of lead bromide in silver bromide at this temperature has an observed molal volume of 50.32, which is identical with that calculated on the basis of additivity.

Discussion of Results

To show the effect of both temperature and composition upon the properties of the solutions, Fig. 1 was plotted on a large scale and the values of the e. m. f. determined for each composition at the temperatures 450, 500 and 550° by noting the intersections of the curves with these temperature ordinates. By applying the usual thermodynamic equations[3] to these e. m. f.'s, values have been calculated for the free energy of formation of silver bromide from solid silver and bromine vapor, ΔF_1, the free energy of dilution or the partial molal free energy, $\bar{F}_1$, the entropy change, ΔS_1, and the partial molal entropy, $\bar{S}_1$, the heat of formation, ΔH_1, the activity of silver bromide in the solutions taking pure silver bromide as the standard state, a_1, and the activity coefficient, a_1/N_1, where N_1 is the mole fraction of silver bromide.

These values are given in Table III, and Fig. 2, curve C, shows the partial molal free energy, $-\bar{F}_1$ at 500°, plotted against log $(1/N_1)$.

In order to compare this observed curve with that calculated on the assumption that Raoult's law is obeyed it may be assumed, first, that both salts are un-ionized. Then the partial molal free energy is given by the equation, $\bar{F}_1 = RT \ln N_1$, where $N_1 = a_1$. This gives curve B, Fig. 2, which agrees perfectly with the observed results up to a half mole fraction of added lead bromide. With increasing concentration of lead bromide there is a slight but increasing positive deviation of the activity of silver bromide from Raoult's law, since a_1/N_1 becomes greater than unity. However, even at the maximum concentration of lead bromide (0.9 mole fraction) the calculated partial molal free energy of silver bromide is only 110 calories more than the observed. To make sure that these small deviations were not fortuitous, the cells were carefully checked. Their respective

[5] Lorenz and Höchberg, *Z. anorg. allgem. Chem.*, **94**, 288 (1916).

[6] Lorenz, Frei and Jabs, *Phil. Trans. Royal Soc.*, **7**, 468 (1908).

TABLE III

ENERGY RELATIONS OF FUSED LEAD BROMIDE–SILVER BROMIDE SOLUTIONS

N_1	1.00	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00[a]
$dE/dt \times 10^6$ (volt/deg.)	−290	−268	−266	−258	−234	−222	−191	−158	−112	−607
ΔS_1 (cal./deg.)	−6.69	−6.18	−6.14	−5.95	−5.40	−5.12	−4.41	−3.65	−2.58	−28.01
$\bar{s}_1$ (cal./deg.)	0	0.51	0.55	0.74	1.29	1.57	2.28	3.04	4.11	0
450°, E (volt)	0.8010	0.8149	0.8238	0.8336	0.8446	0.8580	0.8733	0.8976	0.9407	1.0624
450°, ΔF_1 (cal.)	−18480	−18800	−19010	−19230	−19490	−19800	−20150	−20710	−21710	−49030
450°, $\bar{F}$ (cal.)	0	−320	−530	−750	−1010	−1320	−1670	−2230	−3230	0
450°, a_1	1.000	0.800	0.692	0.594	0.495	0.399	0.313	0.212	0.106	
450°, a_1/N_1	1.00	1.00	0.99	0.99	0.99	1.00	1.04	1.06	1.06	
500°, E (volt)	0.7865	0.8015	0.8106	0.8207	0.8328	0.8470	0.8637	0.8897	0.9352	1.0321
500°, ΔF_1 (cal.)	−18150	−18490	−18700	−18940	−19220	−19540	−19930	−20530	−21580	−47630
500°, $\bar{F}_1$ (cal.)	0	−340	−550	−790	−1070	−1390	−1780	−2380	−3430	0
500°, ΔH_1 (cal.)	−23320	−23270	−23440	−23540	−23390	−23500	−23340	−23350	−23580	−69280
500°, a_1	1.000	0.801	0.699	0.600	0.500	0.404	0.314	0.213	0.107	
500°, a_1/N_1	1.00	1.00	1.00	1.00	1.00	1.01	1.05	1.06	1.07	1.08
550°, E (volt)	0.7720	0.7882	0.7972	0.8078	0.8212	0.8358	0.8542	0.8818	0.9295	1.0017
550°, ΔF_1 (cal.)	−17810	−18190	−18390	−18640	−18950	−19290	−19710	−20350	−21450	−46230
550°, $\bar{F}_1$ (cal.)	0	−380	−580	−830	−1140	−1480	−1900	−2540	−3640	0
550°, a_1	1.000	0.794	0.700	0.603	0.500	0.406	0.313	0.212	0.108	
550°, a_1/N_1	1.00	0.99	1.00	1.01	1.00	1.02	1.06	1.06	1.08	

[a] These values are for the cell: Pb(l), $PbBr_2$(l), Br_2(g).

temperature—e. m. f. curves agreed within 0.2 millivolt which would correspond to a deviation of ±5 calories in the partial molal free energy.

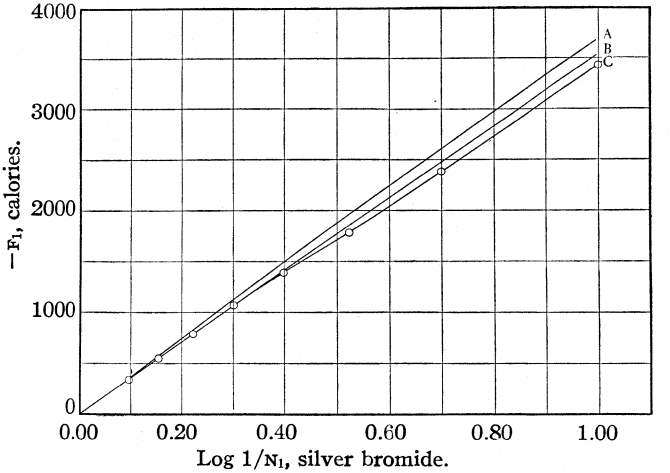


Fig. 2.—Change in free energy of silver bromide at 500° upon dilution with lead bromide: C, observed; A, calculated on the basis of complete ionization of both salts; B, calculated on the basis of no ionization.

If it is assumed, second, that Raoult's law is obeyed and that both salts are completely ionized, but that the partial substitution of silver by lead ion can be made without changing any of the interionic forces, then if n_1 moles of silver bromide and n_2 moles of lead bromide are taken, there will then be n_1 moles of Ag^+, n_2 moles of Pb^{++} and $n_1 + 2n_2$ moles of Br^-. The activity of Ag^+ would then be $2n_1/(2n_1 + 3n_2)$, the activity of Br^-, $2(n_1 + 2n_2)/(2n_1 + 3n_2)$, and the activity of silver bromide, the product of the two, or

$$a_1 = 4n_1(n_1 + 2n_2)/(2n_1 + 3n_2)^2$$

The $-\bar{F}_1$ calculated on this basis, curve A in Fig. 2, is found to be too high.

Since the deviation of the activity of silver bromide from Raoult's law though small is undoubtedly real, it is believed worth while to calculate the activity of the solute, namely, lead bromide, in the solutions. This may be done by employing the general partial molal equation[7] showing for any infinitesimal alteration in composition at constant temperature and pressure, the relation between the change in any one partial molal quantity and the change in all others, namely

$$N_1\left(\frac{\partial \bar{G}_1}{\partial N_1}\right)_{P,T} + N_2\left(\frac{\partial \bar{G}_2}{\partial N_2}\right)_{P,T} + \ldots\ldots = 0$$

[7] *Cf.* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 43.

where $\bar{G}_1$ and $\bar{G}_2$ are any partial molal quantities. Introducing the free energy into this equation and choosing the standard state of lead bromide in the solution at infinite dilution, *i. e.*, $a_2/N_2 = 1$ when $N_2 = 0$, this general equation may be brought into the form

$$\log a_2/N_2 = -\int_0^{N_2} \frac{N_1}{N_2} \, d \log \frac{a_1}{N_1}$$

In general when the above equation is integrated graphically by plotting N_1/N_2 against $\log a_1/N_1$ the difficulty is encountered that N_1/N_2 rapidly approaches infinity as N_2 approaches zero. However, in this case it is not necessary to go beyond the value of 1.0 for N_1/N_2, for from this point on Raoult's law is obeyed, *i. e.*, $a_1/N_1 = 1$, and its logarithm is therefore zero.

By such graphical integration the activity, a_2, and activity coefficient, a_2/N_2, of lead bromide were obtained. By using the equation $\bar{F}_2 = RT \ln a_2$ the partial molal free energy, $\bar{F}_2$, of lead bromide was also calculated, which when added to the free energy of formation of fused lead bromide[3] from molten lead and bromine vapor yields ΔF_2. The values so obtained are given in Table IV and Fig. 3, curve A, shows $-\bar{F}_2$ plotted against log $(1/N_2)$. To see how this agrees with Raoult's law it may be assumed first, that both salts are un-ionized. Calculation of $-\bar{F}_2$ on this basis gives curve C, Fig. 3, which agrees very well with the observed results, the maximum positive deviation being less than 80 calories.

TABLE IV

THERMODYNAMIC RELATIONS OF FUSED LEAD BROMIDE–SILVER BROMIDE SOLUTIONS

N_2	a_2	a_2/N_2	$\bar{F}_2$	ΔF_2
		At 500°		
1.000	0.962	0.962	0	−47630
0.900	.873	.970	− 150	−47780
.800	.782	.978	− 320	−47950
.700	.692	.988	− 510	−48140
.600	.598	.996	− 730	−48360
.500	.500	1.000	−1010	−48640
.400	.400	1.000	−1350	−48980
.300	.300	1.000	−1790	−49420
.200	.200	1.000	−2410	−50040
		At 550°		
1.000	0.959	0.959	0	−46230
0.900	.871	.967	− 160	−46390
.800	.781	.977	− 340	−46570
.700	.690	.986	− 540	−46770
.600	.597	.995	− 780	−47010
.500	.500	1.000	−1070	−47300
.400	.400	1.000	−1430	−47660
.300	.300	1.000	−1900	−48130
.200	.200	1.000	−2600	−48830

If it is assumed, second, that both salts are completely ionized and that the partial substitution of lead by silver ion can be made without changing any of the interionic forces, then if n_1 moles of AgBr and n_2 moles of $PbBr_2$ are taken there would be n_2 moles of Pb^{++}, n_1 moles of Ag^+ and $2n_2 + n_1$ moles of Br^-. The activity of Pb^{++} would then be $3n_2/(3n_2 + 2n_1)$, the activity of Br^- would be $3(2n_2 + 1)/2(3n_2 + 2n_1)$ and the activity of lead bromide the former times the square of the latter, or

$$a_2 = 27n_2(2n_2 + n_1)^2/4(3n_2 + 2n_1)^3$$

Such calculations are represented by curve B, Fig. 3, which is slightly higher than that calculated on the basis of no ionization.

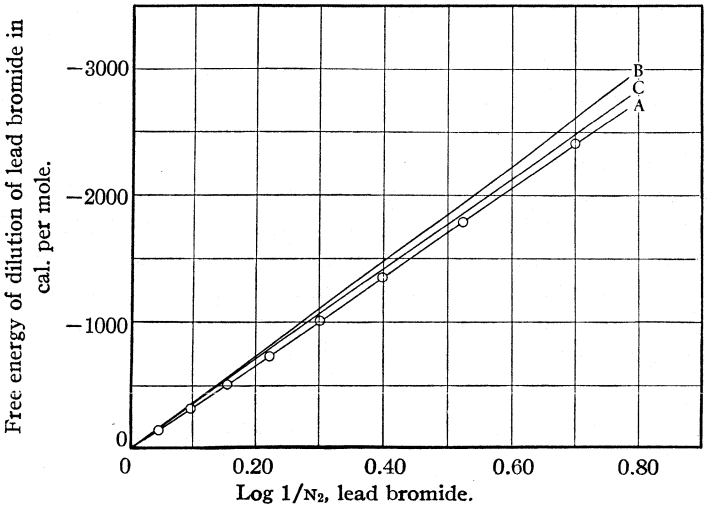


Fig. 3.—Change in free energy of lead bromide at 500° upon dilution with silver bromide: A, observed; B, calculated on the basis of complete ionization of both salts; C, calculated on the basis of no ionization.

It is thus evident that the observed free energies of dilution of both silver bromide (Fig. 2) and lead bromide (Fig. 3) agree very well with that calculated on the basis that Raoult's law is obeyed if it is assumed that both salts are un-ionized, while they agree less well with that calculated on the assumption that both salts are completely ionized. However, the calculations of $\bar{F}$ based on these two assumptions hardly differ sufficiently to warrant a choice between them. The activity coefficients of the two salts in Tables III and IV also show that this close agreement with Raoult's law is not a fortuitous one at a single temperature but persists practically unchanged throughout the whole range of temperature studied. These considerations coupled with the fact that the molal volume of the solution is additive make it clear that we are dealing here with a system that conforms very closely with the perfect solution laws.

Summary

1. Measurements of the e. m. f. of the cell, Ag(s), AgBr(l), $PbBr_2$-(l), Br_2(g) have been made at mole fractions of silver bromide varying from 1.00 to 0.10 between the temperatures 425 and 575°.

2. Densities of a 0.5 mole fraction solution of lead bromide in silver bromide are given by the relation $d^t = 6.243 - 0.00146t$ between the temperatures 490 and 580°.

3. The relations between composition and free energy, heat of formation, entropy change and activity coefficient of the solvent, fused silver bromide, have been calculated for 450, 500 and 550°.

4. The relations between composition and free energy and activity coefficient of the solute, fused lead bromide, have been calculated at 500 and 550°.

5. The activities of both solvent and solute agree very well with that predicted by Raoult's law throughout the entire range of temperature studied.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

QUANTUM MECHANICS OF ACTIVATED ADSORPTION

BY ALBERT SHERMAN AND HENRY EYRING

RECEIVED FEBRUARY 29, 1932 PUBLISHED JULY 6, 1932

The experiments of Taylor and Sherman[1] showed that activated adsorption is involved in the ortho–para hydrogen conversion at a variety of surfaces. On charcoal the activation energy must be small—approximately 2 kg. cal.—since the conversion occurs at liquid hydrogen temperatures.[2] The conversion on a given charcoal surface was shown by Taylor and Sherman to be bimolecular at room temperatures, and the surface action exhibited a temperature coefficient less than unity between liquid air temperatures and 0°. It becomes a matter of considerable interest to apply the methods used by Eyring and Polanyi[3] for calculation of activation energies to determine the necessary conditions for so low an activation energy. The calculations presented in the following pages seem sufficiently accurate to indicate clearly the process by which the reaction proceeds, although, of course, the exact numerical results are subject to revision.

The mechanism for the conversion of ortho to para hydrogen on charcoal probably involves three steps: (1) activated adsorption; (2) collision

[1] Taylor and Sherman, *Trans. Faraday Soc.*, Symposium on Adsorption (1932).

[2] Bonhoeffer and Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

[3] Eyring and Polanyi, *ibid.*, **B12**, 279 (1931).

and reaction of two adjacently adsorbed hydrogen molecules; (3) desorption. At very low temperatures step 3, a zero order evaporation process, is undoubtedly the rate determining step. We should thus expect at intermediate temperatures a transition between second and zero order reactions. As the temperature increases, the rate of desorption increases until finally the collision of two adjacently adsorbed molecules is the slow process. With increasing temperature the chance of two hydrogen molecules being adsorbed in adjacent positions approaches zero and simultaneously the conversion of para to ortho hydrogen drops to zero, in keeping with the results of Taylor and Sherman. It is obvious, therefore, that the rate must go through a maximum when the specific reaction rate k is plotted against the absolute temperature T.

Such a temperature variation is probably general for any catalytic reaction involving a collision between adsorbed molecules. The negative slope portion of the curve may not be realizable experimentally in many cases because the temperature at which the maximum occurs may be such as to destroy the catalyst. The part with positive slope may not be realizable because it may correspond to temperatures below the melting point of the reactants. The known experiments of the conversion of ortho to para hydrogen on charcoal correspond only to the part for higher temperatures than that for which the maximum occurs. In the case of a particular sample of a copper catalyst for this same reaction results lying on both sides of the maximum have been found. In the case of ZnO only that portion of the curve with positive slope was realized.

Adsorption Process.—It has already been pointed out that the activation energy E_a of adsorption of hydrogen on charcoal must be very small. This reaction may be represented as indicated in Fig. 1. The surface carbon atoms, of course, have additional bonds which are not indicated.

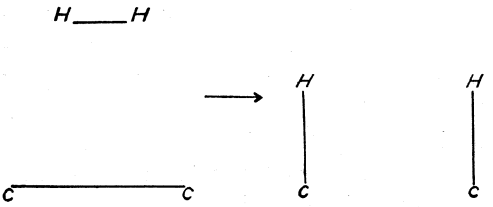


Fig. 1.—Adsorption process.

Since analogous processes are involved in the hydrogenation of ethylene and acetylene we shall first calculate an approximate activation energy for these reactions. For the purposes of these calculations the C—C distances in ethylene and acetylene were taken equal to that in ethane, 1.54 Å. The effective strength of the C—C bond broken was taken as the difference between the strengths of a double and single bond, 123 − 73.5 = 49.5 kg. cal., in the first case and in the second case as the difference between the strength of a triple and double bond, 162 − 123 = 39 kg. cal. The data used for constructing the Morse potential energy curves for C—H and H—H are given in Table I.

TABLE I

Bond	ω, cm.$^{-1}$	r_0 (Å.)	D (kg. cal.)
C—H	2920[a]	1.13[d]	92[c]
H—H	4262[d]	0.76[d]	101.5[d]
C=C	1623[b]	1.54	123[e]
C≡C	1960[b]	1.54	162[e]

[a] Andrews, *Phys. Rev.*, **36**, 538 (1930).
[b] Kettering, Shutts and Andrews, *ibid.*, **36**, 531 (1930).
[c] Eucken, "Handbuch der Experimental Physik."
[d] "International Critical Tables," Vol. V.
[e] Taylor, "Treatise on Physical Chemistry," 1931, p. 328.

The expression for the binding energy of four atoms is

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \sqrt{\tfrac{1}{2}[(\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2]} \quad (1a)$$

where the italic letters are the coulombic potentials corresponding to the six possible distances between four atoms and the Greek letters are the interchange potentials for these same distances. The method of calculation was to construct a potential energy surface for configurations in which the C—C distance was kept at 1.54 Å., the four atoms were kept in a plane, and only configurations symmetrical about the perpendicular bisector of the line joining the two carbon nuclei were considered. Certain of these assumptions have already been discussed[4] and they are considered in greater detail in a forthcoming paper by Kimball and Eyring.

The activation energies for the hydrogenation of ethylene and acetylene were calculated to be 51.5 and 46.4 kg. cal., respectively, at 0°K. The former value is to be compared with 43.2 kg. cal. recently obtained by Pease.[5] The discrepancy is probably due to the operation of several factors. The experimentally measured value is for a temperature of approximately 700°K.,[6] while the calculated value is of course for 0°K. The effect of directed valence will also be to lower the activation energy but we have not attempted a precise evaluation of the magnitude of this lowering. The choice of 10% for the coulombic energy is only approximately correct, although it is probably not greatly in error.

We now consider the analogous process of the reduction of two carbon atoms on a catalytic surface by hydrogen. This is essentially what happens when we have activated adsorption of hydrogen on a charcoal surface. The adsorption process replaces a single bond of 101.5 kg. cal. between the hydrogen atoms and a weaker one between the carbon atoms by two C—H bonds whose combined strength does not exceed by more than approximately two kilogram calories the strength of the two bonds

[4] Eyring, THIS JOURNAL, **53**, 2537 (1931).
[5] Pease, *ibid.*, **54**, 1876 (1932).
[6] Tolman, "Statistical Mechanics," Chemical Catalog Company, New York, 1927, Chap. 21.

broken. If the same potential energy curves are used for this calculation as are used for the hydrogenation of ethylene and acetylene, the upper curve in Fig. 2 is obtained, showing how the activation energy of adsorption changes with the distance between the two carbon atoms. The carbon to carbon bond broken was taken as the difference between a triple and double bond at the appropriate distance. The minimum is not shifted if the carbon to carbon bond broken is assumed instead to be a single bond. On the extreme left where the change would be most marked the curve would be raised by 5 kg. cal. Thus the exact nature of this carbon to carbon bond is not significant for our considerations. The curve shows that

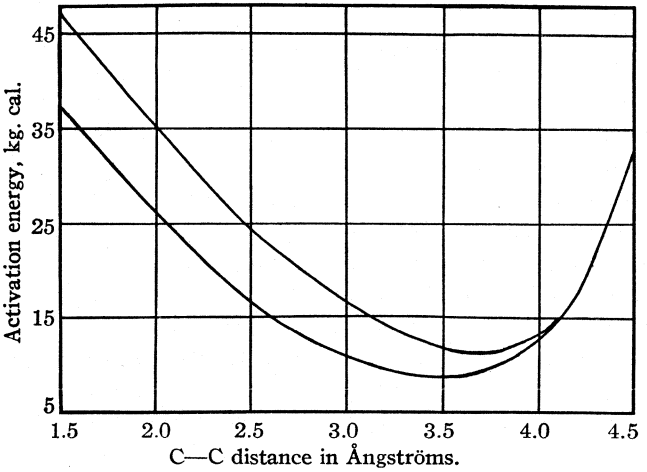
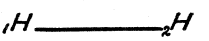


Fig. 2.—The dependence of the activation energy for adsorption of H_2 on charcoal as a function of the distance between surface carbon atoms.

the reaction proceeds with the lowest activation energy for carbon atoms held at a distance of 3.6 Å. The calculated potential surface for the carbon–carbon distance of 3.6 Å. has a minimum which represents the hydrogenation of the carbon atoms with an evolution of 90.5 kg. cal. Actually, as stated previously, hydrogen is adsorbed on charcoal with the liberation of but two kilogram calories, so that there must be forces in the surface preventing the formation of C—H bonds of 96 kg. cal. Since the calculations indicate the adsorption obtained is the so-called atomic adsorption—that is, adsorption in which the hydrogen–hydrogen distance becomes very large—the C–H bonds must have strengths of 51.8 kg. cal. in order that the final bonds will have strengths of only two kg. cal. more than the initial hydrogen bond. We then have the problem of calculating the activation energy for C—H bonds of 51.8 kg. cal. The remaining constants used in the Morse curve are the same as those previously used. Proceeding exactly

as before we obtain the lower curve in Fig. 2. Surprisingly enough, in this case also we find that a carbon–carbon distance of approximately 3.6 Å. is most favorable. This is particularly satisfactory in that it indicates the existence of a most favorable carbon–carbon distance which is practically independent of our choice of the strength of the C—H bond.

That a most favorable carbon–carbon distance is to be expected may be seen from the following qualitative argument. Consider the following two extreme distances between surface atoms. In one case suppose the distance between surface atoms A–A is equal to that of the approaching hydrogen molecule, as illustrated in Fig. 3. In Fig. 3 the subscripts preceding the atomic symbols are used to distinguish the various atoms. In this case there is a large interaction between ${}_3A$ and ${}_2H$ and also between ${}_4A$ and ${}_1H$. As can be seen from Equation (1a), making the smallest interchange integrals (those between diagonal atoms) larger decreases the total binding energy, thus making the activation energy larger.



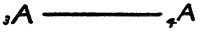


Fig. 3.—If the distance A–A is equal to that between the atoms adsorbed, the activation energy will be high.

Now consider the case in which the surface atoms are very far apart. In this case all the terms in Equation (1a) except those between the two hydrogen atoms are small and this distance must also become very large in order that the hydrogen atoms can be adsorbed. This process, then, is essentially a dissociation of a hydrogen molecule and necessitates an activation energy of approximately 100 kg. cal. Thus, somewhere between these two extremes a most favorable distance of A–A is to be expected. We see that there are no reasons for the assumption sometimes made that it is favorable for the distance between surface atoms to be equal to that of the molecule being adsorbed.

The potential energy surface for the adsorption of hydrogen on two carbon atoms at 3.6 Å. is given in Fig. 4.

Similar surfaces were obtained for other C–C distances used in constructing Fig. 2. These resemble those shown in Fig. 4 and so are not reproduced.

The height of the pass in Fig. 4 separating the valley (corresponding to a hydrogen molecule and two unoccupied carbon atoms) and the basin (corresponding to the two carbon hydrides) is seen to be 8.8 kg. cal. The position of the pass is for an abscissa of 0.77 Å. and an ordinate of 0.80 Å. The course of the hydrogen molecule in the adsorption process is indicated by the arrows in Fig. 4. The activation energy for the desorption of hydrogen will be greater than this by the heat of adsorption, which we have taken to be 2 kg. cal. To agree with experiment we should have obtained 0 kg. cal. for the activation energy instead of 8.8 kg. cal. Thus

again, as in the case of the hydrogenation of ethylene, the value obtained for the activation energy is approximately 9 kg. cal. too high. The arbitrary assumption in our calculation is the choice of 10% for the coulombic energy. A slightly higher value for the coulombic energy would have brought closer agreement in both hydrogenation cases as well as for the adsorption process. Taking into account directed valence also tends to lower the activation energy.

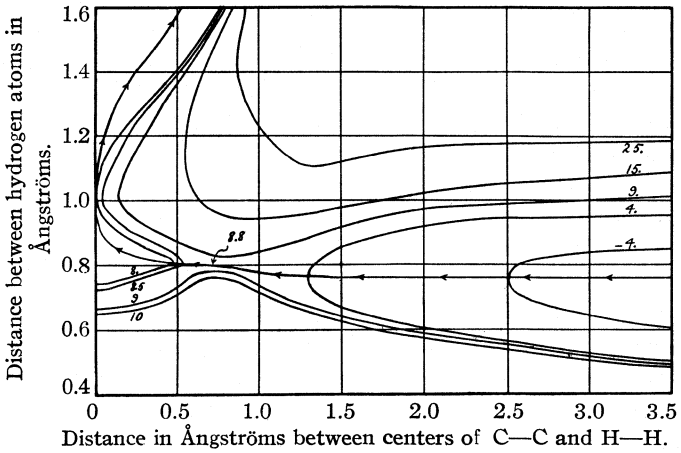


Fig. 4.—Energy contour lines in kg. cal. for the activated adsorption of H_2 on two carbon atoms 3.6 Ångströms apart.

The coulombic energy is known by calculation for the following three cases: H_2, 10% of the total binding;[7] Li_2, 22%;[8] Na_2, 28.3%.[9] If we determine the percentage of coulombic binding for C–H and C–C (14%) by the condition that the calculated value of the activation energy shall agree with the value found experimentally by Pease for the hydrogenation of ethylene, the adsorption of hydrogen on charcoal may be redetermined. Instead of the value of 8.8 kg. cal., we now obtain 5.6 kg. cal., in better agreement with experiment.

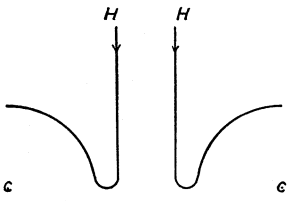


Fig. 5.—Path followed by H_2 when becoming adsorbed on charcoal.

An examination of Fig. 4 shows that the path of the hydrogen atoms as they approach the carbon atoms is of the kind schematically represented in Fig. 5. It is interesting to note that H_2 approaches the carbon–carbon axis before expanding appreciably.

For desorption the path will be just the reverse of that of adsorption.

[7] Sugiura, *Z. physik*, **45**, 484 (1927).

[8] Bartlett and Furry, *Phys. Rev.*, **37**, 1712 (1931).

[9] Rosen, *ibid.*, **38**, 255 (1931).

It might be supposed that it would require a greater activation energy for a second hydrogen molecule to be adsorbed on two carbon atoms adjacent to the pair on which the first hydrogen molecule is adsorbed because of the repulsion of the first two hydrogen atoms already adsorbed. This is not so, however, because of the large distance between the carbon atoms. Thus the activation energy for the successive adsorption of two adjacent hydrogen molecules is just that for the individual processes in this case where the four carbon atoms form a square.

It may be assumed that the actual mechanism for the catalytic conversion of para to ortho hydrogen is not the one just considered but one in which a hydrogen molecule from the gas phase collides with an adsorbed hydrogen molecule. A consideration of this involves solving the six electron problem, one from each of the four hydrogen atoms and one from each of the two carbon atoms, and will be discussed in connection with Table II. The fifth degree equation (4) for the binding energy of six electrons must be used for calculating the potential energy. The value for the elements of this determinant are given in (20) below.

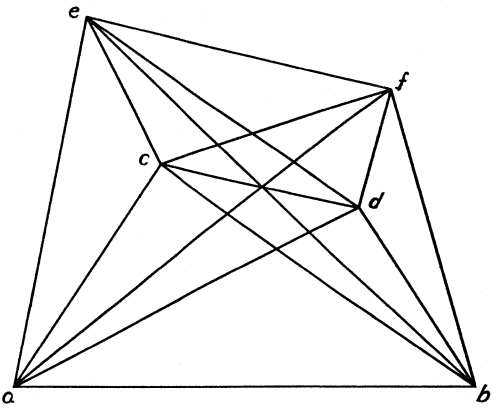


Fig. 6.—The potential curves for pairs of atoms connected by lines determine the potential for the whole configuration.

We shall now discuss the evaluation of the activation energy for any configuration such as is indicated in Fig. 6.

At the corners of the quadrilateral cdef are four hydrogen atoms having the four eigenfunctions c, d, e, f. For the two carbon atoms we have the two eigenfunctions a and b. The energies corresponding to the fifteen distances between the six atoms are evaluated from the same curves used in the previous calculations. We have assumed as before that the coulombic binding energy is 10% of the total binding energy for each pair of atoms. This enables us to evaluate each of the elements in (4) without further difficulty. We then try values for E until we find the numerically largest negative number which satisfies (4). This corresponds to the singlet state of lowest potential energy. In Table II are given the data and resulting binding energies for three configurations.

In Table II, E is the potential energy required to break completely all the bonds between the six atoms.

In configurations 1, 2 and 3 all the atoms lie in a plane and there is symmetry about the perpendicular bisector of the C—C bond. First

TABLE II

Configuration	1 Dist.	1 Coul.	1 Inter.	2 Dist.	2 Coul.	2 Inter.	3 Dist.	3 Coul.	3 Inter.
ab	2.60	0.4	3.1	3.26	0.0	0.0	3.26	0.0	0.0
ac	1.13	5.4	48.8	1.13	5.4	48.8	1.24	5.1	45.6
ad	1.97	1.3	11.2	2.25	0.7	6.6	2.28	0.7	5.8
ae	1.97	1.3	11.2	1.51	3.4	30.8	1.24	5.1	45.6
af	2.54	0.3	3.0	2.44	0.4	3.9	2.28	0.7	5.8
bc	1.97	1.3	11.2	2.23	0.7	6.6	2.28	0.7	5.8
bd	1.13	5.4	48.8	1.13	5.4	48.8	1.24	5.1	45.6
be	2.54	0.3	3.0	2.44	0.4	3.9	2.28	0.7	5.8
bf	1.97	1.3	11.2	1.51	3.4	30.8	1.24	5.1	45.6
cd	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
ce	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
cf	1.41	5.5	49.3	1.41	5.5	49.3	1.41	5.5	49.3
de	1.41	5.5	49.3	1.41	5.5	49.3	1.41	5.5	49.3
df	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
ef	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
E		89.6 kg. cal.			73.0 kg. cal.			65.0 kg. cal.	

we may consider the activation energy to bring four hydrogen atoms into a square of 1 Å. on a side, when the carbon atoms are not present. This is 84.2 kg. cal. A square configuration for four atoms of hydrogen is clearly one in which any hydrogen atom is equally apt to depart with either of two neighbors as a partner, so that the square corresponding to the least potential energy is the activated state for the homogeneous ortho–para conversion between two diatomic hydrogen molecules.

Let us now consider the decrease in potential energy for our three configurations of six atoms resulting when we remove the two hydrogen atoms with eigenfunctions e and f to a great distance from the other four atoms but to the normal distance of 0.76 Å. from each other. The other four atoms are held fixed. The decreases in energy are 96.5, 119.8 and 124.5 kg. cal., respectively, for the three configurations. The activation energy for the reverse process will clearly be given by these same figures. Thus it is highly improbable for a second hydrogen molecule to approach an adsorbed hydrogen molecule without the aid of two additional carbon atoms.

Let us next consider the activation energy of four hydrogen atoms in the absence and in the presence of two surface atoms. The activation energy without the surface atoms, as already stated, is 84.2 kg. cal. Instead of being lowered, our calculations for configurations 1, 2 and 3 show that the surface carbon atoms raise this activation energy to the values $2 \times 101.5 - 89.6 = 113.4$, 130.0 and 138.0 kg. cal., respectively.

The process we considered in our first adsorption calculations thus appears to be the true catalytic process. The ortho–para hydrogen conversion has also been discussed recently by Ekstein and Polanyi.[10]

[10] Ekstein and Polanyi, *Z. physik. Chem.*, **B15**, 334 (1932).

The five independent eigenfunctions that we have used in calculating the energy for the six electron problem correspond to five different ways of drawing three bonds, indicated as

ψ_1'	a − b	c − d	e − f
ψ_2'	a − b	c − e	d − f
ψ_3'	a − c	b − d	e − f
ψ_4'	a − c	b − e	d − f
ψ_5'	a − d	b − e	c − f

For a particular set of six monovalent atoms the configuration determines the eigenfunctions associated with each of the energy values which are roots of the secular equation. Thus, if the lowest root of the secular equation is the sum of the heats of dissociation of the three molecular bonds a—b, c—d, e—f, and the three corresponding molecules are remote from each other, the eigenfunction going with this energy is just ψ_2'. As the six monovalent atoms approach each other the binding can no longer be represented simply by three fixed bonds. Thus for the three configurations in Table II we have instead of some one of the eigenfunctions ψ_1' to ψ_5' the following linear combinations

Configuration 1: $0.406\psi_1' + 0.568\psi_2' + 0.694\psi_3' + 0.130\psi_4' + 0.122\psi_5'$.
2: $0.524\psi_1' + 0.432\psi_2' + 0.698\psi_3' + 0.224\psi_4' + 0.019\psi_5'$.
3: $0.757\psi_1' + 0.200\psi_2' + 0.366\psi_3' + 0.355\psi_4' + 0.355\psi_5'$.

The squares of the coefficients of the eigenfunction for each configuration must, of course add up to one. As is well known, the binding energies for most compounds correspond closely to what one calculates if a definite set of bonds is assumed. A chemical reaction consists in passing from a potential minimum corresponding to a single set of bonds such as is represented by ψ_1' or ψ_2', etc., through states of mixed bonds for which the potential energy is higher, such as those corresponding to those of our configurations 1, 2, 3, to a new potential minimum where there is again a single set of bonds.

Molecules involving polyvalent atoms may not reach the ideal state of a single set of bonds because of the mutual interaction of two groups attached to the same atom. This manifests itself as steric hindrance and the eigenfunctions will be of the mixed type just described. Organic molecules never quite have the simple set of bonds ordinarily assigned them.

Bonhoeffer and Farkas[11] suggested that the conversion they observed on platinum could be attributed to the pulling apart of the atoms of hydrogen with a subsequent reunion of these same two atoms upon desorption to form a molecule with a changed resultant nuclear spin. Quantum mechanics indicates that such a process will not occur except as catalyzed by radiation or by other hydrogen atoms. Even if the atoms are separated

[11] Bonhoeffer and Farkas, *Trans. Faraday Soc.*, Symposium on Adsorption (1932).

to great distances by electrostatic forces, they always return with the same resultant nuclear spin they had initially. Only magnetic perturbations can hasten a change in nuclear spin. The following picture illustrates the situation. Suppose one thinks of the two atoms as two ships, each carrying a gyroscopic compass corresponding to nuclear spins. If the compasses point in the same direction when the ships are each proceeding in a given direction and parallel to each other and if the ships then separate to any distance, it will still be found that upon returning to their original relative positions the gyroscopic needles will be parallel. The needles, of course, may have any relative positions to begin with, which is conserved no matter what forces are applied to the ships so long as these forces do not act directly on the compasses.

Bonhoeffer and Harteck in one of their early papers[2] on the ortho–para hydrogen conversion include a discussion by Wigner on the rate at which black body radiation affects the conversion and we have had the opportunity of discussing this question in some detail with Professor Wigner. At ordinary temperatures a half life of approximately 300 years is found for the atoms in s states. If they are in p states the half life is shown to be about twelve hours. Thus to the extent to which a catalytic surface changes the quantum state of the atoms we obtain a greatly increased effect of radiation on the rate of conversion. One can only estimate the magnitude of this change in quantization but it would be surprising if the catalyst raises the binding electrons more than 10% into p states, which would still give us a rate far too low to account for the observed rates of conversion at surfaces. In fact a half life of twelve hours, that for atoms in p states, is too slow to account for the experimental observations on catalytic surfaces.

Because of the apparent success of the present method of attack we are extending our calculations to other surfaces.

We now give the solution of the six electron problem.

To secure the utmost brevity we shall assume familiarity on the part of the reader with a recent paper by Slater[12] in which the problem of spin degeneracy is solved for three and four electrons. We use his notation. The reader desiring a simple and detailed treatment of this problem may be referred to the thesis of one of us on file in the Princeton Library.

The Schrödinger equation for six electrons is approximately satisfied by the product of the six electronic eigenfunctions $a_1 b_2 c_3 d_4 e_5 f_6$, where the numbers specify the electrons and the letters the available eigenfunctions. The 720 different products obtained by permutation of the numbers are all equally good solutions of the Schrödinger equation. Any linear combination of them is also a solution. Taking account of electron spins we write for electron 1 having the positional eigenfunction a and

[12] J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

spin $+1/2$, $(a\alpha)_1$ and for a spin of $-1/2$ the expression $(a\beta)_1$. Now when we use the Pauli principle instead of 720 eigenfunctions in our secular equation we need consider only the 64 antisymmetric eigenfunctions

$$\psi_i = \Sigma \pm p\,(a\alpha)_1(b\alpha)_2(c\beta)_3(d\beta)_4(e\alpha)_5(f\beta)_6 \qquad (1)$$

where $\Sigma \pm p$ signifies the sum of the 720 possible quantities obtained by permutation of the subscripts, using the positive sign if the product may be obtained from the initial product by an even number of interchanges of pairs of subscripts, and otherwise the negative sign (1) may also be written as a determinant. There are just $2^6 = 64$ eigenfunctions of the type (1) since in each of the six parentheses we can insert either an α or β. Terms $\int \psi_i H \psi_j d\tau$ in the secular equation are zero if the sum of the spins in ψ_i is not the same as in ψ_j, where H is the well-known operator for six electrons and the integration is over all the coordinates of the six electrons. This is true because a term of the form

$$\int (a\alpha)_1(b\beta)_2(c\alpha)_3 \ldots (f\alpha)_6 H (a\alpha)_1(b\beta)_2(c\alpha)_3 \ldots (f\alpha)_6 d\tau$$

for which the spin eigenfunctions of every electron before and after H is the same, is equal to $\int a_1 b_2 c_3 d_4 e_5 f_6 H a_1 b_2 c_3 d_4 e_5 f_6 d\tau$, and if for any single electron the spin eigenfunctions are not the same, the integral is identically zero. This causes our 64 rowed secular determinant to break up into the product of seven determinants corresponding to the integral spin values from 3 to -3.

The most stable chemical state will correspond to a state for which the sum of the spins for the six electrons is zero; so that we are only concerned with solving the corresponding twenty rowed determinant. The 20 eigenfunctions may be indicated in the following symbolic fashion

	a	b	c	d	e	f		a	b	c	d	e	f		a	b	c	d	e	f
ψ_{23}	α	α	α	β	β	β	ψ_{30}	α	β	β	α	α	β	ψ_{37}	β	α	β	α	β	α
ψ_{24}	α	α	β	α	β	β	ψ_{31}	β	α	β	α	α	β	ψ_{38}	β	β	α	α	β	α
ψ_{25}	α	β	α	α	β	β	ψ_{32}	β	β	α	α	α	β	ψ_{39}	α	β	β	β	α	α
ψ_{26}	β	α	α	α	β	β	ψ_{33}	α	α	β	β	β	α	ψ_{40}	β	α	β	β	α	α
ψ_{27}	α	α	β	β	α	β	ψ_{34}	α	β	α	β	β	α	ψ_{41}	β	β	α	β	α	α
ψ_{28}	α	β	α	β	α	β	ψ_{35}	β	α	α	β	β	α	ψ_{42}	β	β	β	α	α	α
ψ_{29}	β	α	α	β	α	β	ψ_{36}	α	β	β	α	β	α							

(2)

Here the table indicates with which italic letters in (1) an α or β should be associated. Actually ψ_i of (1) is ψ_{27}.

If now instead of using the 20 eigenfunctions of (2) we had used the 20 given below, which are a linear combination of them, our 20th order determinant now factors into four sub-determinants of orders 5, 9, 5, 1.

$$\psi'_1 = \frac{1}{\sqrt{8}}(\psi_{28} - \psi_{29} - \psi_{30} + \psi_{31} - \psi_{34} + \psi_{35} + \psi_{36} - \psi_{37})$$

$$\psi'_2 = \frac{1}{\sqrt{8}}(\psi_{25} - \psi_{26} - \psi_{30} + \psi_{31} - \psi_{34} + \psi_{35} + \psi_{39} - \psi_{40})$$

$$\psi'_3 = \frac{1}{\sqrt{8}}(\psi_{27} - \psi_{29} - \psi_{30} + \psi_{32} - \psi_{33} + \psi_{35} + \psi_{36} - \psi_{38})$$

$$\psi'_4 = \frac{1}{\sqrt{8}}(\psi_{24} - \psi_{26} - \psi_{30} + \psi_{32} - \psi_{33} + \psi_{35} + \psi_{39} - \psi_{41})$$

$$\psi'_5 = \frac{1}{\sqrt{8}}(\psi_{23} - \psi_{26} - \psi_{28} + \psi_{32} - \psi_{33} + \psi_{37} + \psi_{39} - \psi_{42})$$

$$\psi'_6 = \frac{1}{\sqrt{8}}(\psi_{28} - \psi_{29} - \psi_{30} + \psi_{31} + \psi_{34} - \psi_{35} - \psi_{36} + \psi_{37})$$

$$\psi'_7 = \frac{1}{\sqrt{8}}(\psi_{27} - \psi_{29} + \psi_{30} - \psi_{32} - \psi_{33} + \psi_{35} - \psi_{36} + \psi_{38})$$

$$\psi'_8 = \frac{1}{\sqrt{8}}(\psi_{23} - \psi_{24} - \psi_{28} + \psi_{30} + \psi_{35} - \psi_{37} - \psi_{41} + \psi_{42})$$

$$\psi'_9 = \frac{1}{\sqrt{8}}(\psi_{25} - \psi_{26} - \psi_{30} + \psi_{31} + \psi_{34} - \psi_{35} - \psi_{39} + \psi_{40})$$

$$\psi'_{10} = \frac{1}{\sqrt{8}}(\psi_{28} - \psi_{29} + \psi_{30} - \psi_{31} - \psi_{34} + \psi_{35} - \psi_{36} + \psi_{37})$$

$$\psi'_{11} = \frac{1}{\sqrt{8}}(\psi_{24} - \psi_{26} + \psi_{30} - \psi_{32} - \psi_{33} + \psi_{35} - \psi_{39} + \psi_{41}) \qquad (3)$$

$$\psi'_{12} = \frac{1}{\sqrt{8}}(\psi_{23} - \psi_{26} + \psi_{28} - \psi_{32} - \psi_{33} + \psi_{37} - \psi_{39} + \psi_{42})$$

$$\psi'_{13} = \frac{1}{\sqrt{8}}(\psi_{24} - \psi_{26} - \psi_{30} + \psi_{32} + \psi_{33} - \psi_{35} - \psi_{39} + \psi_{41})$$

$$\psi'_{14} = \frac{1}{\sqrt{8}}(\psi_{24} - \psi_{25} - \psi_{31} + \psi_{32} + \psi_{33} - \psi_{34} - \psi_{40} + \psi_{41})$$

$$\psi'_{15} = \frac{1}{\sqrt{12}}(\psi_{25} - \psi_{26} + \psi_{28} - \psi_{29} + \psi_{30} - \psi_{31} + \psi_{34} - \psi_{35} + \psi_{36} - \psi_{37} + \psi_{39} - \psi_{40})$$

$$\psi'_{16} = \frac{1}{\sqrt{12}}(\psi_{24} - \psi_{26} + \psi_{27} - \psi_{29} + \psi_{30} - \psi_{32} + \psi_{33} - \psi_{35} + \psi_{36} - \psi_{38} + \psi_{39} - \psi_{41})$$

$$\psi'_{17} = \frac{1}{\sqrt{12}}(\psi_{23} - \psi_{26} + \psi_{27} + \psi_{28} - \psi_{31} - \psi_{32} + \psi_{33} + \psi_{34} - \psi_{37} - \psi_{38} + \psi_{39} - \psi_{42})$$

$$\psi'_{18} = \frac{1}{\sqrt{12}}(\psi_{23} + \psi_{24} + \psi_{25} - \psi_{29} - \psi_{31} - \psi_{32} + \psi_{33} + \psi_{34} + \psi_{36} - \psi_{40} - \psi_{41} - \psi_{42})$$

$$\psi'_{19} = \frac{1}{\sqrt{12}}(\psi_{23} + \psi_{24} + \psi_{25} + \psi_{27} + \psi_{28} + \psi_{30} - \psi_{35} - \psi_{37} - \psi_{38} - \psi_{40} - \psi_{41} - \psi_{42})$$

$$\psi'_{20} = (1/\sqrt{20})\sum_{i=23}^{42}\psi_i$$

This new choice is of course permissible since any linear combination of solutions of a Schrödinger equation is still a solution of the equation. The new sub-determinant of order one corresponds to one component of the septet—that is, to no electron pair bonds. The last mentioned 5th order determinant corresponds to the five independent eigenfunctions arising from having one bond among the six electrons. (There are actually fifteen ways of drawing one bond, giving rise to fifteen eigenfunctions, of which not more than five are linearly independent.) Similarly, the 9th and the other 5th order determinants are associated with the independent eigenfunctions arising from drawing two and three bonds, respectively.

The twenty eigenfunctions of (3) thus fall into four non-combining sets—

ψ'_1 to ψ'_5, ψ'_6 to ψ'_{14}, ψ'_{15} to ψ'_{19}, ψ'_{20}. That is, $\int \psi'_i \, H\psi'_{20} d\tau = 0$ for i running from 1 to 19. The eigenfunctions ψ'_{15} to ψ'_{19} combine among themselves but not with those outside the group. The same may be said of the groups ψ'_1 to ψ'_5 and ψ'_6 to ψ'_{14}.

Since we are only interested in the energy corresponding to three bonds we need consider only the determinant arising from the eigenfunctions ψ'_1 to ψ'_5. It is interesting to remark that there are actually fifteen ways of drawing three bonds and therefore 15 eigenfunctions, of which not more than five are linearly independent. Any linearly independent set of five would have served our purpose as well as the set we chose.

Actually the way of forming the eigenfunctions (3) from the set given in (2) is important; for no bonds one simply takes a sum of the twenty eigenfunctions. An eigenfunction for six electrons corresponding to a bond between a and b is obtained by taking a linear combination of the twelve eigenfunctions in the set (2) for which the spins of a and b are opposite. Those for which a is associated with α are taken with a plus sign and those for which a is associated with β are taken with a minus sign. For convenience in calculation we divide by a normalizing factor $\sqrt{12}$. The eigenfunction corresponding to a bond between a and b is ψ'_{15} of (3).

To obtain an eigenfunction with two bonds, say one between a and b and one between c and d, we select a linear combination of the eigenfunctions from (2) which have different spins for a and b and at the same time different spins for c and d. If a particular eigenfunction is taken as positive, *e. g.*, ψ_{28}, then the sign of any other is positive if the spins associated with a, b, c and d may be made the same as those in ψ_{28} by interchanging the spin eigenfunctions of a and b and simultaneously those of c and d. If it is obtained by only one of these interchanges, it is negative. In this case we divide by a normalizing factor $\sqrt{8}$. The eigenfunction just described is ψ'_6. There are 45 eigenfunctions corresponding to drawing two bonds, of which not more than 9 are linearly independent.

For the case of three bonds connecting the eigenfunctions a to b, c to d, and e to f a linear combination of all eigenfunctions from (2) is chosen in which the spin associated with each atom of these three pairs is different from its partner. If for an arbitrary one, ψ_{28}, a plus sign is taken, the sign of any other one of the 8 is positive if it may be obtained from ψ_{28} by an even number of spin interchanges between atom pairs, and negative if by an odd number. The eigenfunction here described is ψ'_1.

With more than six electrons exactly the same scheme as outlined above can be used for obtaining an eigenfunction corresponding to an arbitrary number of bonds.

In evaluating our determinant for the singlet state we shall make certain approximations. We shall neglect energy integrals corresponding to more than two electrons jumping simultaneously. When all the atoms

are far apart the electronic eigenfunctions are strictly orthogonal. We shall neglect the fact that this is no longer true as the atoms approach each other. A partial correction for this results automatically from the fact that we use spectroscopic potential curves for evaluating the energy integrals.

The 5th order determinant for the singlet state can be written symbolically as follows

$$\begin{vmatrix} H'_{11}-Ed'_{11} & H'_{12}-Ed'_{12} & H'_{13}-Ed'_{13} & H'_{14}-Ed'_{14} & H'_{15}-Ed'_{15} \\ H'_{12}-Ed'_{12} & H'_{22}-Ed'_{22} & H'_{23}-Ed'_{23} & H'_{24}-Ed'_{24} & H'_{25}-Ed'_{25} \\ H'_{13}-Ed'_{13} & H'_{23}-Ed'_{23} & H'_{33}-Ed'_{33} & H'_{34}-Ed'_{34} & H'_{35}-Ed'_{35} \\ H'_{14}-Ed'_{14} & H'_{24}-Ed'_{24} & H'_{34}-Ed'_{34} & H'_{44}-Ed'_{44} & H'_{45}-Ed'_{45} \\ H'_{15}-Ed'_{15} & H'_{25}-Ed'_{25} & H'_{35}-Ed'_{36} & H'_{45}-Ed'_{45} & H'_{55}-Ed'_{55} \end{vmatrix} = 0 \qquad (4)$$

where $H'_{ij} = \int \psi'_i H \psi'_j d\tau$ and $d'_{ij} = \int \psi'_i \psi'_j d\tau$.

The separate terms of the determinant are given below. The following notation is used: $ac = \int a_i H c_j dx_i dy_i dz_i dx_j dy_j dz_j$. Thus ac is the interchange integral between the eigenfunctions a and c, with similar definitions for other terms. Also Q is defined as

$$Q = \int a_1 b_2 c_3 d_4 e_5 f_6 H a_1 b_2 c_3 d_4 e_5 f_6 d\tau \qquad (5)$$

Any permutation of the electrons in (5) applied both to the electronic eigenfunctions before and after H does not change the value of the integral. Q is really the sum of the 15 Coulombic integrals between pairs of eigenfunctions—that is, between the atoms if all the atoms are monovalent.

The terms are

$$\begin{aligned} d'_{11} &= d'_{22} = d'_{33} = d'_{44} = d'_{55} = 1 \\ d'_{12} &= d'_{13} = d'_{24} = d'_{34} = d'_{45} = 1/2 \\ d'_{14} &= d'_{23} = d'_{25} = d'_{35} = 1/4 \\ d'_{15} &= -1/4 \end{aligned}$$

$$\begin{aligned} H'_{11} &= Q + ab + cd + ef - 1/2[ac + ad + ae + bc + bd + be + bf + cf + ce + de + df + af] \\ H'_{22} &= Q + ab + ce + df - 1/2[ac + ad + cd + be + bf + ef + af + cf + bd + de + ae + bc] \\ H'_{33} &= Q + ac + bd + ef - 1/2[ab + ae + be + cd + cf + df + af + bf + de + ce + ad + bc] \\ H'_{44} &= Q + ac + be + df - 1/2[ab + ad + bd + ce + cf + ef + af + bf + cd + de + ae + bc] \\ H'_{55} &= Q + ad + be + cf - 1/2[ab + ac + bd + ce + df + ef + af + bf + cd + de + ae + bc] \\ H'_{12} &= \frac{Q}{2} - cf - de - 1/2\left[\frac{ad + ae + bc + bf + ac + af + bd + be}{2} - df - ce - ef - cd - ab\right] \\ H'_{13} &= \frac{Q}{2} - bc - ad - 1/2\left[\frac{af + df + cf + bf + de + be + ce + ae}{2} - cd - ef - ab - bd - ac\right] \\ H'_{24} &= \frac{Q}{2} - bc - ae - 1/2\left[\frac{ad + de + bf + cf + af + ef + bd + cd}{2} - be - ac - ce - df - ab\right] \\ H'_{34} &= \frac{Q}{2} - bf - de - 1/2\left[\frac{ab + af + cd + ce + ae + bc + cf + ad}{2} - df - be - ef - bd - ac\right] \\ H'_{45} &= \frac{Q}{2} - af - cd - 1/2\left[\frac{ab + bf + ce + de + ae + ef + bc + bd}{2} - cf - df - be - ac - ad\right] \\ H'_{14} &= 1/4Q + 1/4[be + af + bd + ef + cd + ac + ab + ce + df - 2(ae + bf + bc + ad + de + cf)] \\ H'_{23} &= 1/4Q + 1/4[bd + af + be + ac + ce + df + ab + ef + cd - 2(bf + ad + bc + ae + de + cf)] \\ H'_{25} &= 1/4Q + 1/4[bf + ad + be + ac + de + cf + ce + df + ab - 2(bd + af + bc + ae + ef + cd)] \\ H'_{35} &= 1/4Q + 1/4[cf + ae + ef + bd + ac + bc + ad + be + df - 2(ce + af + ab + bf + cd + de)] \\ H'_{15} &= -1/4Q - 1/4[be + af + bc + ad + ef + cd + ab + cf + de - 2(ae + bf + bd + ac + ce + df)] \end{aligned} \qquad (6)$$

Thus for monovalent atoms all the quantities in (4) are determined if we know the Coulombic and interchange integrals between atom pairs.

We wish to express our thanks to Professor Taylor for helpful suggestions in connection with this paper.

Summary

1. It is pointed out that in general for bimolecular surface reactions a plot of the specific reaction rate against the temperature will exhibit a maximum.

2. The quantum mechanical calculations of the activation energies for the hydrogenation of ethylene, acetylene and the activated adsorption of hydrogen on charcoal are given. If the Coulombic binding is taken as 10% of the total for all atom pairs the activation energy is approximately 9 kg. cal. too high in all cases. The significance of this result has been discussed.

3. It is shown that a most favorable distance of carbon-carbon atoms in charcoal exists (approx. 3.6 Å.) such that the activation energy for adsorption is a minimum.

4. The calculations indicate a probable mechanism for the ortho–para hydrogen conversion and point to the improbability of the following three possible mechanisms: (a) a conversion resulting from the dissociation of a single molecule of hydrogen by surface carbon atoms (with subsequent recombination), in the absence of a neighboring hydrogen molecule; (b) the lowering of the activation energy of the homogeneous reaction of two hydrogen molecules due to the presence of two surface carbon atoms; (c) a collision of a hydrogen molecule from the gas phase with an adsorbed hydrogen molecule. This case differs from (b) only that in (c) we assume that two of the hydrogen atoms come much closer to the surface than the other two atoms.

5. The problem of spin degeneracy of six electrons is solved and the equation for the potential energy applied to the calculation of activation energies.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 287]

THE FREEZING POINTS OF AQUEOUS SOLUTIONS. I. A FREEZING POINT APPARATUS

BY GEORGE SCATCHARD, P. T. JONES AND S. S. PRENTISS[1]

RECEIVED MARCH 2, 1932 PUBLISHED JULY 6, 1932

I. Introduction

The most accurate method of determining the chemical potential or activity of the solvent in very dilute solutions, and the most convenient method in moderately dilute ones, is the measurement of freezing point depressions. The method is applicable whenever the solid phase in equilibrium with the solution is the pure solvent, and is therefore very general. Except where unusually accurate electromotive force measurements in very dilute solutions are possible and in a few other special cases, the most accurate way to determine the chemical potential of the solute is to compute it from that of the solvent. For these reasons an extensive program of freezing point measurements has been inaugurated in our laboratory.

With modern thermocouples and accessories it is possible to measure small freezing point depressions with an accuracy which we estimate as about two hundred-thousandths of a degree centigrade. Some observers quote figures to a two-hundredth of this quantity, but the discussion which follows will explain our estimate. As the molal freezing point depression of water is 1.858°, this means that the freezing point depression of a hundredth molal solution can be measured to one-tenth of a per cent., and that of a thousandth molal solution to one per cent. These figures refer to the total number of solute molecules. For an electrolyte the concentration at which a given accuracy may be attained should be divided by the number of ions corresponding to one molecule of the electrolyte. The chief disadvantage of freezing points for thermodynamic calculations is that the temperature at which the chemical potential of the solvent is measured varies with the composition. For this reason, and because the measurements in concentrated solutions require a different technique, we have taken approximately one molal as the upper limit of our measurements on salt solutions. The accuracy of the temperature measurements sets a thousandth molal as the practicable lower limit.

In the "equilibrium method" of measuring freezing points the problem is to maintain ice and the solution at equilibrium, and to determine the temperature and composition as accurately as possible. We believe that our measurements are accurate to the larger of the two quantities: one

[1] This and the two following articles are abstracts of parts of the theses submitted to the Massachusetts Institute of Technology by P. T. Jones and S. S. Prentiss in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

two-thousandth of the freezing point depression, or one fifty-thousandth of a degree centigrade. To attain this precision demands careful consideration of several points. We shall describe the apparatus from the point of view of the objects to be met. In most respects our apparatus resembles one or another of those recently described,[2] but in some respects it differs from any known to us.

II. The Freezing Point Vessels and Stirrers

Only differential measurements can attain the above accuracy. Therefore the apparatus consists of two vessels, matched as closely as possible in every respect, one of which contains ice and water, the other ice and the solution. At first silver vessels were used, but, since these tarnished somewhat, the surfaces which came into contact with the solutions or water were later gold-plated.

The vessels are cylindrical with hemispherical bottoms, 8 cm. in diameter and 20 cm. deep. The interior is divided into three compartments by two parallel vanes so arranged that the center compartment is 4 cm. wide, and the two side compartments are 2 cm. wide at the center. The center compartment is the equilibrium vessel proper and contains all the ice. The side compartments are the pump "cylinders." As closely as possible to the bottom of each side compartment is a hinged valve which occupies the whole cross section of the compartment. To allow the free circulation of the liquid several holes, 0.2 cm. in diameter, are bored in the semicircular end of the vanes below the valves. The other end of each vane is cut off 3 cm. from the top of the vessel. To prevent ice from falling back into the pumps, this free space is filled with a silver collar into which 0.3–0.4 cm. holes are bored as closely together as possible. The pump pistons are valves similar to the fixed ones, but supported in a wire frame. All parts of the pumps are of silver heavily plated with gold. The construction of the vessels and pumps is shown by Fig. 1.

The stirring must serve two purposes. The first is to bring all the solution into contact with the ice, and the second is necessitated by the pressure effect on the freezing point of water. The freezing point of water is lowered 0.0075° per atmosphere, or eight millionths of a degree per cm. head of water. To attain an accuracy of two hundred-thousandths of a degree the depth of immersion of the two thermometers must be the same to 2 cm. The set up of the apparatus ensures that the difference in depth is not more than a fifth this large. More serious is the fact that the equilibrium temperature is sixteen hundred-thousandths of a degree higher at the top of the apparatus than at the bottom because of the 20 cm. difference in level. The temperature at any point in the apparatus must be an integrated mean of the equilibrium temperatures at different levels, whose relation to the freezing point at any level must depend upon the nature of the stirring. To obtain the same integration in each vessel to ten per cent. of the temperature range, the vessels must be matched as closely as possible, and the amount of

[2] The more important papers discussing modern technique are: (a) Roloff, *Z. physik. Chem.*, **18**, 572 (1895); (b) Walker and Robertson, *Proc. Roy. Soc. Edinburgh*, **24**, 363 (1902); (c) Osaka, *Z. physik. Chem.*, **41**, 560 (1902); (d) Richards, *ibid.*, **44**, 563 (1903); THIS JOURNAL, **25**, 241 (1903); (e) Flügel, *Z. physik. Chem.*, **79**, 577 (1912); (f) Adams, THIS JOURNAL, **37**, 481 (1915); (g) Hall and Harkins, *ibid.*, **38**, 2658 (1916); (h) Harkins and Roberts, *ibid.*, **38**, 2676 (1916); (i) Rodebush, *ibid.*, **40**, 1204 (1918); (j) Randall and Vanselow, *ibid.*, **46**, 2418 (1924); (k) Hovorka and Rodebush, *ibid.*, **47**, 1614 (1925); (l) Randall and Scott, *ibid.*, **49**, 636 (1927); (m) Karagunis, Hawkinson and Damköhler, *Z. physik. Chem.*, [A] **151**, 431 (1930); (n) Robertson and La Mer, *J. Phys. Chem.*, **35**, 1953 (1931).

liquid circulated must be nearly independent of differences in friction due to different packing of the ice, but the stirring must not be turbulent enough to produce local differences of pressure with consequent differences in freezing point.

We believe that valve pumps attain these objectives more efficiently than turbine or gas-lift stirrers. The volume of liquid circulated is practically independent of the friction, the stirring is smooth, with two pumps it is almost continuous, and there is very little heat produced by friction. In our apparatus two strokes of each pump are required to circulate a volume equal to that of all the liquid in the apparatus. It is operated at a rate of twenty-five strokes of each pump per minute. The operation is so smooth that channels appear to form between the ice particles, causing slow drifts in the temperature. This difficulty is obviated by the use of a hand-operated glass ring stirrer which is operated for a few strokes some minutes before each reading.

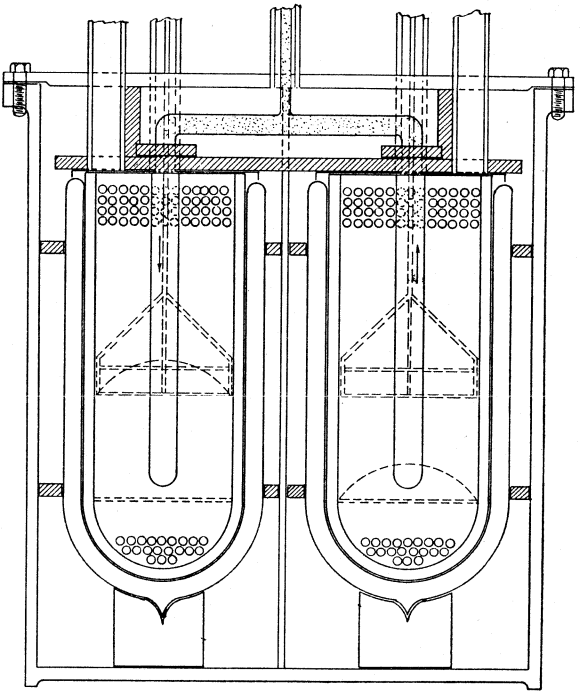


Fig. 1.—Freezing point apparatus.

III. The Containing Apparatus

Any heat added to the vessels either from the stirring or from the outside goes largely to melting the ice, and therefore causes dilution and a change in the equilibrium temperature on the solution side. So it is desirable to make the operation as nearly adiabatic as possible. To accomplish this, the vessels are placed in silvered Dewar flasks which fit snugly, and the Dewars are placed in a cylindrical box, 31 cm. high and 24 cm. in diameter, which is divided through the center, between the vessels, by a 3-mm. iron plate. Each Dewar rests on a large cork and is held in place by two hard rubber shelves which are supported by the iron plate and two small brass legs on the outer side. The cover of this box is bolted on with twelve bolts and the joint made tight with a rubber gasket. From the cover five iron tubes 13 mm. in internal diameter, and two 16 mm. in diameter, project

32 cm. The two larger tubes open above the equilibrium vessels and permit the insertion of pipets, gas tubes and hand stirrers. Four of the smaller tubes are for the pump rods. The fifth at the center of the box contains the lead wires to the thermoelements. All but the last of these tubes were plated on the inner surface with copper and then with silver. These tubes also serve to suspend the box from the cover of the thermostat, which is a can 64 cm. high and 50 cm. in diameter, thoroughly insulated to save ice.

To the lower side of the box cover is attached a hard rubber box, 16.5 cm. long, 5.1 cm. wide, and 3.2 cm. high, with a bottom which projects to form a roof over both vessels. The thermoelements are supported from this roof and the wires connecting the two pass through the box. Above each vessel is a silver lid with a flange which extends outside the vessel, completely protecting but not touching it. The lids and the roof are bored with holes to fit the thermocouples and the openings for the stirrers and pipets.

The stirring mechanism consists of two brass wheels mounted on the same axis as a sprocket wheel which is connected to a reducing gear driven by an electric motor. Each wheel is so connected by a piston to a bar sliding on two perpendicular steel rods that the two bars move in opposite phases. Each sliding bar is connected by a brass rod with a stirrer in each vessel. The connection from the brass rod to the silver-wire frame of the stirrer is through a hard rubber rod 10 cm. long which fits rather closely in the silvered tube. The two vessels are thus stirred synchronously, and in each vessel one stirrer rises as the other falls.

When the apparatus is in use the thermostat can is filled with chopped ice and water, which cover the iron box and surround the lower 15 to 18 cm. of the tubes. The equilibrium vessels are thus quite completely surrounded by an environment at 0°, and they are furthermore well insulated from it. Except through the Dewar flasks and the gas, the vessels are in contact with other bodies only through the stirrers, the pipet tubes, glass stirrers and gas entry tubes and the thermocouples. Any heat leak through the thermocouples is so much more important to the temperature reading that it will be discussed under that head. The lids of the vessels practically prevent convection and therefore any disturbance due to heat leak through the gas. The stirrers are insulated by the 10-cm. rubber rods which are cooled nearly to zero degrees. The glass stirrers and tubes are also cooled nearly to zero degrees by contact with the silvered tubes and are such poor heat conductors that they should carry very little heat into the vessels.

The effect of the sum of the heat added by the stirring and by leakage can be determined for the concentrated solutions, where it gives a measurable change in the equilibrium temperature. This was found to be 0.02% of the freezing point depression per minute. The technique of these measurements was such as to make this the limiting value of a more rapid change from a lower freezing point. Since the removal of a sample for analysis requires only half a minute, and the temperature readings are extrapolated to the time when half the sample has been removed, any error from this cause is negligible. The only other observers who have reported such data for their apparatus are Karagunis, Hawkinson and Damköhler,[2m] who found a change of 0.05% per minute.

IV. The Effect of Dissolved Gases

At zero degrees the solubility of nitrogen in water is 0.001 *M* and that of oxygen is twice as great, so that the dissolved gases cannot be ignored. Their effect on the freezing point has been discussed by Hall and Harkins,[2g] Randall and Vanselow,[2j] Karagunis, Hawkinson and Damköhler,[2m] and Robertson and La Mer,[2n] but never completely. Because of salting out, the solubility of these gases in salt solutions is less than in water when the gas is at the same pressure, that is, at the same chemical potential

or activity. It has been customary to consider that the contribution of the gas to the freezing point depression is nevertheless proportional to its concentration.

A more accurate treatment shows that this contribution is more nearly proportional to the activity, which remains constant. We shall designate the solvent water by the subscript 1, the salt by 2, and the gas by 3. We shall assume that at any one salt concentration the gas obeys Henry's law, and that the change in chemical potential of the gas is proportional to the mole fraction of the salt at constant mole fraction of the gas. There has been no experimental test of the first assumption but, since the maximum mole fraction of nitrogen is less than one fifty-thousandth, it is highly probable. The second assumption has been found approximately valid up to salt concentrations of several molal.

We may express these assumptions by the equation

$$\frac{\partial F}{\partial n_3} = RT \ln x_3 + A + B \frac{n_2}{n_1 + \nu n_2} \tag{1}$$

where F is the free energy, x_3 the mole fraction of the gas, ν the number of ions corresponding to one molecule of salt, and A and B are constants. Then

$$F = RT\Sigma n_i \ln x_i + n_3 A + B \frac{n_2 n_3}{n_1 + \nu n_2} + f(n_1, n_2) \tag{2}$$

$$\frac{\partial F}{\partial n_1} = RT \ln \frac{n_1}{n_1 + \nu n_2 + n_3} - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2} + \frac{\partial f(n_1, n_2)}{\partial n_1} \tag{3}$$

Letting the subscript 0 refer to $n_2 = 0$

$$\left(\frac{\partial F}{\partial n_1}\right)_0 = RT \ln \left(\frac{n_1}{n_1 + n_3}\right)_0 + \left(\frac{\partial f(n_1, n_2)}{\partial n_1}\right)_0 \tag{4}$$

$$\frac{\partial F}{\partial n_1} - \left(\frac{\partial F}{\partial n_1}\right)_0 = RT \ln \frac{n_1}{n_1 + \nu n_2 + n_3} - RT \ln \left(\frac{n_1}{n_1 + n_3}\right)_0 - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2} + \frac{\partial f(n_1, n_2)}{\partial n_1} - \left(\frac{\partial f(n_1, n_2)}{\partial n_1}\right)_0 \tag{5}$$

When $n_3 = 0$ but the ratio n_2/n_1 is unchanged

$$\frac{\partial F}{\partial n_1} - \left(\frac{\partial F}{\partial n_1}\right)_0 = RT \ln \frac{n_1}{n_1 + \nu n_2} + \frac{\partial f(n_1, n_2)}{\partial n_1} - \left(\frac{\partial f(n_1, n_2)}{\partial n_1}\right)_0 \tag{6}$$

The difference is

$$\Delta \left[\frac{\partial F}{\partial n_1} - \left(\frac{\partial F}{\partial n_1}\right)_0\right] = \Delta = RT \ln \frac{n_1 + \nu n_2}{n_1 + \nu n_2 + n_3} - RT \ln \left(\frac{n_1}{n_1 + n_3}\right)_0 - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2}$$

$$= RT \ln \frac{1 - x_3}{1 - (x_3)_0} - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2} \tag{7}$$

and combining with equation (1), remembering the constancy of $\partial F/\partial n_3$, we obtain

$$\Delta = RT \left[\ln \frac{1 - x_3}{1 - (x_3)_0} - \frac{n_3}{n_1 + \nu n_2} \ln \frac{(x_3)_0}{x_3}\right] \tag{8}$$

So far there have been no approximations. We may take advantage of the fact that x_3 is very small to obtain

$$\Delta = RT\left[(x_3)_0 - x_3\left(1 + \ln\frac{(x_3)_0}{x_3}\right)\right]$$
$$= RT\,(x_3)_0\,[z + (1 - z)\ln(1 - z)] \quad (9)$$
$$= RT\,(x_3)_0\left[\frac{z^2}{2} + \frac{z^3}{6} + \ldots\ldots\ldots\right] \quad (10)$$

where z is the fraction of the gas salted out. Returning to equation (1) we find that

$$z = 1 - \frac{x_3}{(x_3)_0} = 1 - e^{-\frac{B}{RT}\frac{n_2}{n_1 + \nu n_2}} \leqq \frac{B}{RT}\frac{n_2}{n_1 + \nu n_2} = \frac{55.5\,B}{RT}\,m = \beta m \quad (11)$$

Combining with equation (10)

$$\Delta \leqq RT\,(x_3)_0\left[\frac{\beta^2 m^2}{2} + \frac{B^3 m^3}{6} + \ldots\ldots\right] \quad (12)$$

The simpler theory hitherto used gives

$$\Delta = RT(x_3)_0\,[z] \leqq RT(x_3)_0\,[\beta m] \quad (13)$$

Since z cannot be greater than unity, the complete theory always gives a smaller value than equation (13), and for dilute solutions it gives a very much smaller value. The value in brackets in equation (10), (12) or (13) multiplied by the freezing point depression of the solution of the gas in water at the given pressure gives the error in the freezing point depression due to this effect. For nitrogen this depression is about 0.002°, and the value of β with sodium chloride is $^1/_3$. With the simpler theory one calculates an error of about 0.02% for all concentrations; the more complete theory gives 0.001% for a molal solution, and even smaller values for lower concentrations. Even for polyvalent ions, for which the relations are less favorable, the effect is much smaller than the experimental error.

There is a second effect due to the change in solubility with the temperature. The solubility of nitrogen increases 2% for each degree drop in temperature; the corresponding change in the freezing point is 0.004%. Since this tends to give too large a depression it tends to compensate the salting out effect. Since each effect is much smaller than the experimental error, it is certain that their difference is also much smaller.

It is essential, however, that the degree of saturation be the same in the two vessels to about 1% of the solubility at one atmosphere. This may be most easily attained when the total pressure is one atmosphere on each side and the gas is bubbled through enough to ensure equilibrium. In our experiments we use nitrogen because it is less soluble than air and because it is chemically inert.

V. The Measurement of Temperature

A multiple thermocouple is the instrument best adapted to the accurate measurement of small temperature differences. The copper–constantan couple is well adapted to this purpose because its temperature coefficient of electromotive force is large, and because both kinds of wire can be obtained with constant properties. We use a 48 element couple of double silk wound No. 36 copper and No. 30 constantan wire. It

consists of two completely independent 24 element couples, each of which is made up of four groups of six elements each, with a wire to the head between each group and at the extremes. Thus a group of 6, 12, 18 or 24 elements from each couple may be used independently, in series, or in opposition. At the head the lead wires are soldered to copper screws whose thread ends project through the lid of the head and are fitted with copper nuts. Connection with the potentiometer circuit is made through No. 14 copper wire with copper leads fastened between two of these nuts. It was found desirable to pack this head in cotton wool to prevent sudden changes in temperature.

Much time and annoyance can be saved in constructing a thermocouple by the method of White[3] by the simple expedient of driving a series of nails in the board an inch or two beyond the section required and winding the wires on these nails without cutting. After the wires are clamped in place they are cut and the parts which had been wrapped around the nails are rejected.

The electromotive force is measured by a Leeds and Northrup "White potentiometer" covering 10,000 microvolts (μv) in steps of 1 μv, and their HS galvanometer constructed to fit the 236 ohms resistance of the thermocouple. The fractions of a microvolt are determined from the galvanometer deflections measured on a scale six meters distant. With all 48 elements two hundred-thousandths of a degree corresponds to about 0.04 μv and to about 0.6 mm. on the scale. There is no difficulty in making readings much more closely than this, but it is about twice the accuracy claimed by the makers. However, since the most important difficulty is from parasitic electromotive forces, there is every indication that with an all-copper circuit and with lagging to prevent temperature changes at all junctions, the temperature of the thermocouple heads can be determined with this accuracy.

The maintenance of the thermocouple heads at the same temperature as the solution demands further consideration. It is essential to make the thermal conductance from the solution to the heads as large as possible relative to the conductance from the heads to the outside either through the thermocouple wires or through the support and casing. Since the temperature of the solution changes only very slowly, the thermocouple need not respond very quickly to changes of temperature. The problem is thus essentially different from that of a thermocouple for calorimetry.

Our thermocouples are illustrated in Fig. 2. The outside shell is of platinum, 16 cm. long, 13 mm. in diameter and 0.25 mm. thick. This contains a close fitting brass core with eight longitudinal grooves (A) 2.5 mm. deep and 1.5 mm. wide to conduct the wires, and with a band 2.5 mm. deep cut out from B to C to contain the thermocouple heads. The core is also cut down to 5 mm. from D to E and from F to G, and the space filled with a similarly grooved core of hard rubber. The upper rubber core spreads to a head through which the wires pass, which serves to hold the whole in place. The spaces within the platinum tube are filled with paraffin. We found the method of filling under vacuum to be unsatisfactory because of the

[3] White, THIS JOURNAL, **36**, 2292 (1914).

excessive shrinking of paraffin on solidification. The cores which had been so treated to impregnate the insulation were then dipped in paraffin. When this had cooled the shells were slipped on, shearing off excess paraffin.

The brass core and platinum shell are in intimate contact over a large area and should therefore be at the same temperature. The thermometer head is essentially the brass core from D to the tip, for the thermocouple heads are in a band only 2.5 mm. deep between two metal surfaces and should have the same temperature as the bulk metal.

Any thermal contact except with the solution must be upward through the 5-mm. brass rod, the hard rubber core, the platinum shell and the thermocouple wires. The purpose of the section from E to F is to bring all these, particularly the wires, to the temperature of the solution well above the thermometer head. This section is constructed just as the head itself, and the surface of contact with the solution is twenty-five times the cross-sectional area. The top is in thermal contact with a box in the same way that the bottom is with the thermometer head.

Within the box the wires are bound to a hard rubber rod to prevent any sharp bend. All joints are covered with a thick coating of picein and the box is filled with paraffin. This box is in contact with the cover of the iron vessel, and is therefore at approximately zero degrees. The only contact with the outside is through the ten copper wires which lead to the thermocouple head.

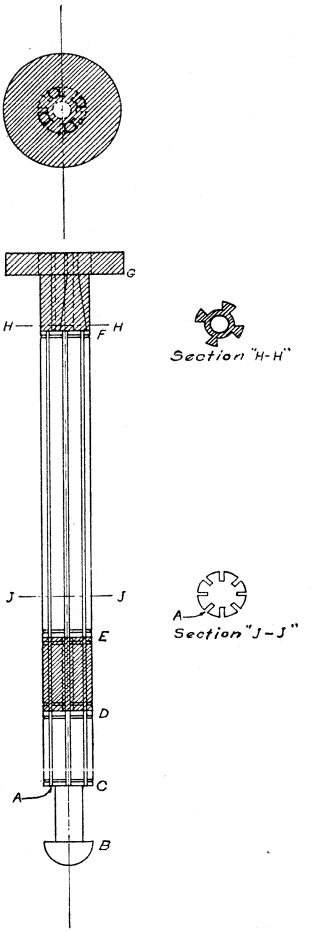


Fig. 2.—Thermocouple core.

Any remaining uncertainty due to the conduction of heat to the thermocouple may be further reduced by making the calibration under conditions as nearly as possible identical with those of the freezing point measurements. Exact duplication is impossible because no other method gives sufficiently exact temperatures. Our thermocouple was calibrated by inserting in one vessel a four-lead platinum resistance thermometer,[4] and measuring the freezing point depression of sodium nitrate solutions from one to ten degrees with the conditions, except for the presence of the resistance thermometer and the larger depressions, just as in our freezing point measurements. The vessel

[4] Beattie, Jacobus and Gaines, *Proc. Am. Acad. Arts Sci.*, **66**, 167 (1930).

was somewhat shallow for the resistance thermometer used. With pure water–ice in the vessel and water–ice in the outside thermostat it gave the same ice point as when completely immersed. When the ice and water were removed from the thermostat and the temperature of the iron vessel was 20°, the reading was +0.016°. With the assumption that this difference is proportional to the difference in temperature between the outer bath and the thermometer head, the platinum resistance temperature was corrected by multiplying by 1.0008.

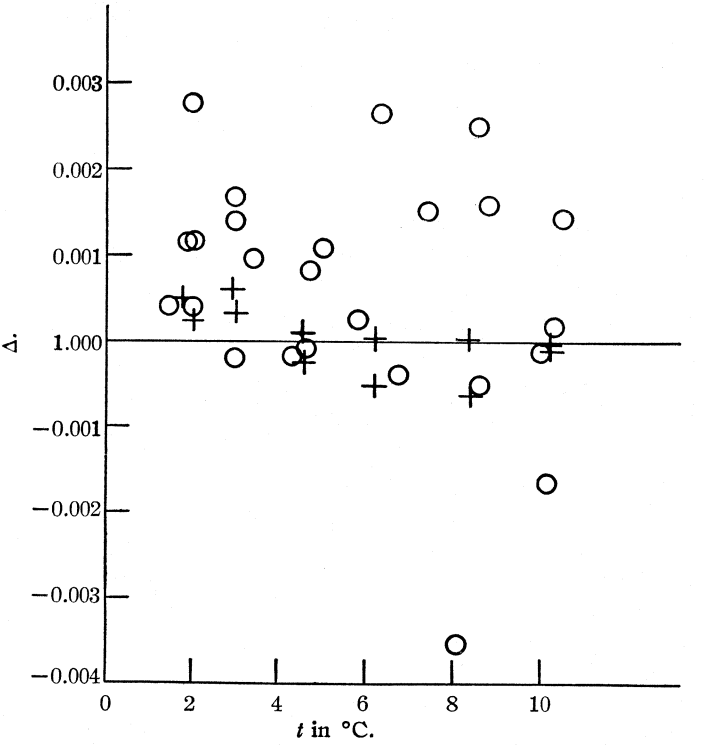


Fig. 3.—Calibration of thermocouple: +, old thermocouple; ○, new thermocouple.

The usual method is to calibrate the thermocouple at two points from 20 to 40° each side of the ice-point and to express the results by a quadratic or two-constant exponential equation. The difference between these two forms is not inappreciable over this temperature range, and there is no evidence that the electromotive force follows either within the precision demanded. Our temperatures do depend upon the accuracy of the Callendar formula for the platinum resistance thermometer, which Hening[5]

[5] Hening, *Ann. Physik*, **40**, 647 (1913); Hening and Heuse, *Z. Physik*, **23**, 105 (1924).

has checked to his accuracy of 0.01° down to −40°, but they can readily be corrected to any other formula if a better one is determined, for they do not depend on the properties of any particular thermocouple.

The relation between the freezing point depression θ and the electromotive force E is expressed by the equation $\theta = 5.385 \times 10^{-4} E + 3.7 \times 10^{-10} E^2$, whose constants were determined by the method of least squares. Figure 3 shows the deviations from this equation of four series of measurements of the thermocouple we used in the freezing point measurements and of two measurements with another couple made from the same reels of wire. For the more concentrated solutions it was necessary to take separate readings on each half of the couple. The fact that no difference could be detected between the readings of the two halves, and the agreement between the readings of the two thermocouples, indicate the homogeneity of the wires. These experiments also showed that the temperature lag of our thermocouple is very nearly the same as that of a "strain-free" platinum resistance thermometer.

VI. The Determination of the Concentration

The concentration is determined by measuring the electrical conductance of the solutions. This method has the advantage that, except for very dilute solutions where the water correction becomes large, the relative error is practically independent of the concentration. Since only 50 cc. of solution is available for rinsing and filling the conductance cells, these must have a small volume. Such cells are not adapted to accurate measurement of the absolute conductance of dilute solutions. Otherwise the cells correspond to the best practice at the time they were built (1927); but today we would have built them with a greater distance between the filling tubes and the connections to the opposite electrode. These deficiencies probably introduce a small error in the determination of the absolute conductance. Since this error should be the same for the standard solutions as for an unknown of the same concentration, it should not affect the determination of the concentration from the conductance.

The cells are of the customary U shape with one arm swollen into the electrode vessel, and have glass stoppers at the ends of the filling tubes. They are made of Jena glass 16 III. The first contains a volume of 9 cc., has a cell constant of 146.892 at 10°, and has heavily platinized electrodes; the second has a volume of 12 cc., a cell constant of 2.5153, and lightly platinized electrodes; the third has a volume of 20 cc., a cell constant of 0.008369, and sand-blasted platinum electrodes. To obtain such a cell constant with so small a volume is rather difficult. The electrodes are three coaxial cylinders, 4 cm. high and 0.7, 1.1 and 1.5 cm. in diameter, held in fixed relative position by three accurately ground quartz rods between each pair. The outer and inner cylinders are connected together as

one electrode so that both surfaces of the middle cylinder are utilized. Figure 4 shows a sketch of this cell.

Since the solutions are saturated with nitrogen at 0° and any excess gas is likely to separate as inconvenient bubbles at the electrodes, it is desirable to measure the conductance of the solutions at as low a temperature as possible.[6] We attempted an ice-bath and a water–ice-bath, but were not able to obtain accurate temperature control without too large capacity effects. The thermostat is made of four galvanized iron cans with a heavy wooden cover. The inner can is a twelve liter oil-bath; between this and the second is a 5.1 cm. air space; between the second and third, 15 cm. of water and coarsely chopped ice; and between the third and fourth, 13 cm. of insulation. The thermoregulator is mercury in iron, annular in shape, and with a rapidly operated turbine stirrer on the inside and a bare constantan wire heating coil at the top of the inside so that the oil passes directly from the coil to the inside of the regulator. This type of regulator has the advantage not only of a large-conducting surface well but also that the expansion or contraction of the inside cylinder acts with that of the mercury. The thermostat is regulated to 10.000 ± 0.002° as read on a Beckmann thermometer, frequently checked against a platinum resistance thermometer and showing no variation greater than 0.005°.

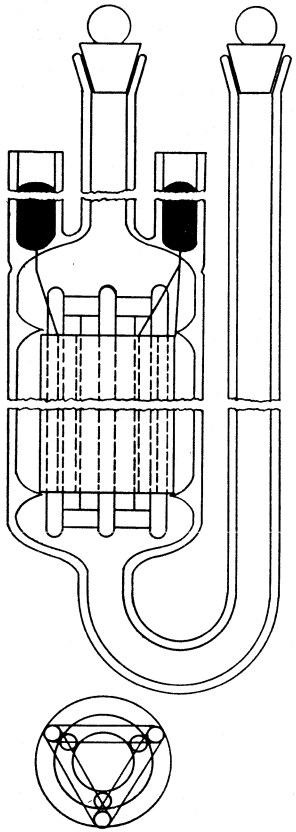


Fig. 4.—Conductivity cell for water.

The conductances are measured on an equal-arm Wheatstone bridge which differs from that of Jones[7] only in a little compactness gained through the elimination of the connections for rapid shifting to direct current. The resistances of 1000 ohms and larger are in a specially made, shielded box with 3.8 cm. between the connecting studs of the ten 1000-ohm coils, and with six 10,000-ohm coils so arranged that when not in use each is entirely disconnected from the system. The resistances are frequently calibrated during the course of the measurements. The source of current is a two-tube push-pull oscillator operated at a frequency of 2700 per second, which seems to be the frequency of greatest

[6] We have made such measurements accurately though not conveniently in an oil thermostat at 30°.

[7] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

sensitivity. The oscillator is five meters distant and connected with shielded wires. The detector system is a two-stage amplifier with telephone.

The first two conductance cells were calibrated with 0.1 M potassium chloride, using the specific conductance of Parker and Parker.[8] To calibrate the third cell, as dilute a solution as possible was measured in the second cell, and then at several frequencies in the third, for the conductance was so great that it varied slightly with the frequency. The resistance was a nearly linear function of the reciprocal of the frequency. The extrapolated value at infinite frequency was used to determine the cell constant. This cell is used only for water, with which there is no detectable variation with the frequency.

A large quantity of concentrated salt solution is prepared and carefully analyzed by a method suitable to the particular salt. More dilute solutions are made by adding weighed amounts of water to weighed amounts of this solution. These solutions are similarly diluted, generally to a tenth, hundredth and thousandth, so that the overlapping of the different series will eliminate any possibility of error from an erroneous weighing. From the resistances of these solutions the specific conductance L is determined, and the ratio of the concentration in moles per kilogram of water M to L. As L/M is an approximately linear function of $\sqrt{M}$, so is M/L an approximately linear function of $\sqrt{L}$. The quantity Δ is determined from the equation

$$\Delta = M/L - A - B\sqrt{L}$$

where A and B are appropriate constants. Δ is plotted against $\sqrt{L}$ on large sheets of cross-section paper such that 1 mm. corresponds to 0.002–0.02%. A smooth curve is drawn through these points, and more values are measured if necessary to determine the curve. From the specific conductance of a solution of unknown concentration it is a simple matter to determine the concentration from the equation and corresponding curve. The conductance measurements and interpolation appear to be accurate to 0.02–0.03%. The largest error in the determination of the concentration is thus in the analysis of the concentrated solution. This method neglects, of course, any change in conductance due to the presence of the nitrogen. Since the mole fraction of nitrogen is always less than 0.00002, it seems that this neglect is justified.

VII. The Procedure

The water used both for freezing point and conductance measurements is doubly distilled, the second time from alkaline permanganate either in our laboratory still or in a small glass still. Its specific conductance is 0.5–0.7 $\times 10^{-6}$ mhos. It is stored in Jena glass bottles. The ice is selected

[8] Parker and Parker, THIS JOURNAL, 46, 312 (1924).

from clear pieces of commercial ice from 0.1–1.0 cm. in size, carefully washed with the doubly distilled water.

Two types of run are made: the first for the more dilute solutions, the second for the more concentrated. The two ranges, however, overlap considerably. For the first the freezing point vessels are filled with ice and water and are placed in the apparatus. Two or three hours are allowed for the attainment of equilibrium with mechanical stirring and a rapid stream of nitrogen. The nitrogen is passed through wash-bottles containing (1) potassium hydroxide solution and (2) pure water, but precooling other than that obtained on passage through the entrance tubes was found unnecessary, since no thermal effects from this cause could be noticed even at rates of bubbling much greater than that used. Then the nitrogen is cut down to about forty bubbles a minute, the ice stirred with the hand stirrer, and a temperature reading is taken after three to five minutes. The stirring and subsequent temperature reading are repeated until several concordant results are obtained. This temperature difference, generally about one hundred-thousandth of a degree, is used as a correction to subsequent readings. Then 50 cc. of water is withdrawn with a pipet from one vessel; its conductance is determined and used as the water correction for the salt solutions. The water is replaced by an equal volume of salt solution of appropriate concentration, the rapid stream of nitrogen started again for about thirty minutes, although there is every indication that equilibrium is attained in five to ten minutes. Then the nitrogen stream is cut down, the stirring and temperature reading are repeated, and a 50-cc. sample is withdrawn for analysis. This is repeated for eight to ten points for each run. The mechanical stirring is continuous throughout the run. At the end the conductance of the water in the other vessel is determined as a check against accidental impurities.

For the second method, one vessel is filled with water–ice and the other with ice and the most concentrated salt solution to be used. One or two hours with a rapid stream of nitrogen is allowed for the first attainment of equilibrium. The procedure is otherwise the same except that water is added instead of solution. The conductance of the water in the other vessel is used as the water correction, and the freezing points are so large that any freezing point correction as applied in the first method would be negligible.

VIII. The Presentation of Data

The Lewis and Randall function $j = 1 - \theta/1.858\nu M$ where θ is the freezing point depression, ν the number of ions corresponding to one molecule of salt, and M is again the number of moles per kilogram of water, is very suitable for the presentation of freezing point data.[9] It is con-

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, pp. 286, 347.

venient for thermodynamic calculations, and has the further advantage that a given relative error makes the same change in j at any concentration. It changes too much, however, to permit sufficiently accurate plotting of j itself. We have chosen to retain the other advantages by plotting the deviation function

$$\Delta_j = j - \frac{A\sqrt{\mu}}{1 + B\sqrt{\mu}} - C\mu$$
$$= j - A\sqrt{\mu} + \frac{AB\mu}{1 + B\sqrt{\mu}} - C\mu$$

where μ is the ionic strength (per kilogram of water) and B and C are empirical constants; A is determined from the theory of Debye and Hückel as 0.3738 times the product of the valence of the ions. From Raoult's law and the value for the heat of fusion of ice, j and Δ_j must be zero when μ is zero. From the theory of Debye and Hückel the tangent of Δ_j plotted against $\sqrt{\mu}$ must be zero when μ is zero. For other concentrations we know only that j, and therefore Δ_j, must be a smooth function of μ. We wish to emphasize that the form of the last two terms does not come from the Debye–Hückel theory and does not even exactly agree with it. We do not pretend that they represent accurately our measurements. They do, however, give a convenient, approximate expression for these measurements. Although j reaches 0.3–0.4, the maximum value of Δ_j is about 0.02. This method permits a very accurate representation of the freezing point measurements even on a small plot, and we will generally use it to smooth our data.

Following Lewis and Randall we will call γ' the activity coefficient—activity divided by the weight molal concentration—calculated from the freezing points with neglect of the generally unknown heat of dilution. Since our temperatures differ from 0° by less than 5°, γ' may be taken as very approximately equal to the activity coefficient at 0°. From the equation of Lewis and Randall we derive

$$-\log \gamma' = 0.4343j + \int_0^M j\alpha \log M = 0.000461 \int_0^\theta (1 - j)\mathrm{d}\theta$$
$$= 0.4343\,(j + C\mu) + \frac{2A}{B}\log(1 + B\sqrt{\mu}) + \int_0^M \Delta_j\,\alpha \log M$$
$$-0.000461 \int_0^\theta (1 - j)\,\mathrm{d}\theta$$

The value of the first integral is obtained analytically from $M = 0$ to $M = 0.001$ by assuming that Δ_j is proportional to M. For higher concentration it is determined graphically by measuring the area under the curve of Δ_j plotted against $\log M$. The last integral, which is always very small, is also obtained graphically.

IX. Summary

The description is given of an apparatus and procedure for the measurement of freezing point depressions by the equilibrium method, in which

the solutions are kept saturated with nitrogen at atmospheric pressure, the concentrations are determined from the conductance and the temperatures with a multiple-junction thermocouple.

The method combines many of what seem to us the best features of previous methods with the following new features: the stirring is done by two low-friction valve pumps in each vessel combined with hand stirring of the ice; the thermocouples are constructed so as to give the smallest possible difference between the temperature of the solution and that of the thermal junctions; the thermocouples are calibrated against a platinum resistance thermometer under conditions as nearly as possible the same as those under which they are used.

It is shown that the effect of dissolved gas is approximately proportional to the square of the salt concentration, and is much smaller than had previously been supposed.

A method of smoothing and computing by use of deviation curves is also described.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 288]

THE FREEZING POINTS OF AQUEOUS SOLUTIONS. II. POTASSIUM, SODIUM AND LITHIUM NITRATES

BY GEORGE SCATCHARD, S. S. PRENTISS AND P. T. JONES

RECEIVED MARCH 2, 1932 PUBLISHED JULY 6, 1932

It has long been known that the charge and "collision diameter" of the ions are not sufficient to explain quantitatively the properties of electrolyte solutions. One of us[1] has discussed the other factors which must enter, and was able to calculate the properties of aqueous solutions of the alkali halides on the assumption that for noble gas type ions the size of each is the only factor which need be taken into account, though this enters in several ways. To extend and test the theory further it is necessary to have accurate data on more complicated ions. For this reason we have measured the freezing point depressions of potassium, sodium and lithium nitrates in the apparatus and with the procedure described in the previous paper.[2]

Lithium nitrate was prepared from lithium carbonate and nitric acid. The potassium and sodium salts were manufacturer's C. P. products. All were crystallized three times from doubly distilled water. The concentrated solutions were analyzed by evaporating to dryness in a platinum crucible, adding sulfuric acid, and igniting to constant weight at dull red

[1] Scatchard, *Physik. Z.*, **33**, 22 (1932).

[2] Scatchard, Jones and Prentiss, Paper I, THIS JOURNAL, **54**, 2676 (1932).

heat. A small piece of ammonium carbonate was added to the potassium sulfate before each ignition to convert any acid sulfate to sulfate. All weights were corrected to vacuum. Except for some results obviously in error due to spattering of acid, the mean deviation from the average of three or four determinations was 0.03–0.04%.

The results of the conductance measurements are given in Table I. The first column gives M, the molality (moles per kilogram of water), the second the ratio of M to the specific conductance L, and the third column this ratio minus the smoothed value at the same L. The freezing point results are given in Table II. The first column is the molality, the second j (= one minus the ratio of the freezing point depression to 3.716 M), and the third the measured j minus the smoothed value. The note gives the temperature difference which corresponds to the third

TABLE I

CONDUCTANCE AT 10°

M	M/L	Diff.	M	M/L	Diff.
		KNO_3			
1.4615	16.619	0.000	0.081233	11.308	+0.016
1.0995	15.582	− .003	.081233	11.307	+ .013
0.93028	15.076	.000	.033518	10.670	− .005
.67706	14.263	− .001	.024071	10.501	− .003
.35013	13.000	.000	.006859	10.037	− .007
.35013	13.074	+ .084	.003544	9.880	− .010
.25008	12.507	− .002	.002268	9.818	+ .006
.18253	12.135	+ .034	.000870	9.688	+ .007
.10552	11.531	+ .007			
		$NaNO_3$			
1.6137	21.184	0.000	0.062877	13.427	0.000
1.2112	19.528	.000	.038031	12.949	− .085
0.91261	18.289	.000	.010775	12.354	+ .003
.70501	17.394	.000	.007714	12.161	− .065
.47661	16.335	− .001	.006852	12.181	− .004
.27393	15.222	.000	.005475	12.026	− .090
.13193	14.196	+ .010	.001002	11.772	.000
.099228	13.854	− .004	.000693	11.709	− .015
.097029	13.845	.000	.000658	11.628	− .090
.083549	13.619	− .075			
		$LiNO_3$			
1.3051	21.462	0.000	0.12327	15.537	−0.002
1.1218	20.679	.000	.077288	15.040	+ .006
0.90837	19.772	.000	.077288	15.033	− .002
.70208	18.858	.000	.042898	14.525	.000
.66323	18.680	.000	.011206	13.724	+ .002
.44114	17.614	.000	.007578	13.559	− .002
.44114	17.652	+ .024	.004482	13.386	+ .001
.32943	17.010	.000	.000899	13.032	− .022
.12327	15.550	+ .012	.000663	12.971	− .047

column for concentrations less than 0.01 M, for which 0.00002° is more than 0.05% of the depression. It will be seen that few of the points lie farther from the smooth curve than the larger of these two quantities.

TABLE II

FREEZING POINTS

M		Diff.[a]	M	j	Diff.
		KNO_3, Series A			
0.001015	0.0217	+0.0103	0.29836	0.1725	0.0000
.001893	.0191	+ .0036	.43511	.2068	− .0002
.006230	.0285	+ .0008	.55577	.2327	− .0005
.016415	.0439	− .0001	.65243	.2521	− .0001
.036379	.0669	+ .0025	.75733	.2711	− .0003
.063274	.0832	− .0003	.88145	.2911	− .0011
.11351	.1097	.0000	1.0010	.3110	.0000
.17737	.1356	+ .0005			
		Series B			
0.90419	0.2974	+0.0014	0.41571	0.2015	−0.0009
.79342	.2780	+ .0003	.28564	.1687	− .0004
.62040	.2452	− .0009	.19567	.1416	+ .0001
		Series C			
0.001081	0.0167	+0.0049	0.058966	0.0812	+0.0004
.003115	.0195	− .0004	.19181	.1399	− .0003
.008291	.0295	− .0023	.36331	.1898	+ .0002
.022811	.0516	.0000			
		$NaNO_3$, Series A			
0.66338	0.1624	0.0000	0.31821	0.1232	−0.0003
.57485	.1539	+ .0001	.22017	.1078	− .0001
.51289	.1476	+ .0002	.15359	.0952	+ .0008
.40414	.1350	.0000			
		Series B			
0.000803	0.0248	+0.0149	0.14163	0.0917	+0.0002
.002096	.0217	+ .0061	.22384	.1083	− .0001
.006389	.0262	+ .0006	1.0742	.1969	+ .0006
.017605	.0394	− .0003	1.1662	.2030	+ .0004
.055233	.0637	+ .0001	0.79637	.1741	− .0001
		Series C			
0.000985	0.0165	+0.0056	0.073695	0.0718	+0.0005
.003101	.0220	+ .0036	.093962	.0788	− .0005
.010875	.0315	− .0008	.19565	.1038	+ .0006
.021100	.0428	− .0001	.24941	.1128	− .0002
.036711	.0539	.0000			
		Series D			
1.6765	0.2314	0.0000	0.73521	0.1684	0.0000
1.3514	.2138	− .0001	.47385	.1432	.0000
0.94282	.1861	− .0003	.36880	.1306	.0002
.84371	.1776	− .0006			

TABLE II (*Concluded*)

M		Diff.[a]	*M*	*j*	Diff.
		$LiNO_3$, Series A			
0.003253	0.0230	+0.0045	0.093540	0.0545	−0.0004
.007473	.0266	+ .0007	.15119	.0573	.0000
.021140	.0377	+ .0003	.22920	.0560	− .0005
.048107	.0488	+ .0012			
		Series B			
0.000632	0.0207	+0.0120	0.037397	0.0450	+0.0004
.001200	.0267	+ .0150	.062754	.0500	− .0006
.002669	.0230	+ .0062	.11718	.0561	− .0001
.007210	.0251	− .0003	.17737	.0574	− .0002
.013703	.0318	− .0005			
		Series C			
1.0501	−0.0066	+0.0006	0.53896	0.0367	+0.0002
0.91557	+ .0051	− .0001	.45022	.0436	+ .0002
.81478	.0141	+ .0003	.37662	.0487	+ .0002
.72572	.0211	− .0002	.29727	.0537	+ .0002
.64424	.0270	− .0011	.20538	.0582	+ .0010
		Series D			
1.1906	−0.0203	−0.0013	0.37301	0.0488	−0.0001
0.92448	+ .0043	− .0002	.25647	.0552	− .0003
.70615	.0229	.0000	.17598	.0579	+ .0003
.55171	.0357	+ .0002			

[a] For concentrations below 0.01 *M* the temperatures in hundred thousandths of a degree, corresponding to the *j* differences are in order: KNO_3, A, 4, 2, 2; C, 2, 0, 7; $NaNO_3$, B, 4, 5, 1; C, 2, 4; $LiNO_3$, A, 5, 2; B, 1, 5, 7, 1.

TABLE III

j VALUES OF THE ALKALI NITRATES

M	Lim. law	KNO_3	$NaNO_3$	$LiNO_3$
0.001	0.0118	0.0114	0.0109	0.0109
.002	.0167	.0159	.0151	.0148
.005	.0264	.0249	.0228	.0218
.01	.0374	.0348	.0311	.0293
.02	.0529	.0485	.0419	.0368
.05	.0836	.0748	.0612	.0480
.1	.1182	.1035	.0803	.0552
.2	.1672	.1429	.1042	.0572
.3	.2047	.1731	.1209	.0533
.4	.2364	.1986	.1345	.0469
.5	.2643	.2214	.1460	.0396
.6	.2897	.2421	.1563	.0317
.7	.3127	.2612	.1656	.0234
.8	.3343	.2788	.1745	.0151
.9	.3546	.2953	.1829	.0066
1.0	.3738	.3109	.1909	− .0021
1.1	.3920	...[a]	.1981	− .0109

[a] KNO_3 eutectic: $M = 1.1396$; freezing point depression = 2.8285; $j = 0.3321$ from preliminary series not otherwise used.

TABLE IV

VALUES OF $-\log \gamma'$ FOR THE ALKALI NITRATES

M	Lim. law	KNO_3	$NaNO_3$	$LiNO_3$
0.001	0.0154	0.0150	0.0146	0.0146
.002	.0218	.0210	.0204	.0201
.005	.0344	.0329	.0311	.0304
.01	.0487	.0461	.0428	.0412
.02	.0689	.0645	.0584	.0543
.05	.1089	.1001	.0870	.0760
.1	.1540	.1391	.1165	.0947
.2	.2178	.1923	.1543	.1125
.3	.2667	.2336	.1812	.1204
.4	.3080	.2677	.2030	.1238
.5	.3444	.2979	.2214	.1246
.6	.3775	.3252	.2378	.1239
.7	.4074	.3502	.2525	.12197
.8	.4356	.3734	.2661	.11931
.9	.4620	.3952	.2788	.1160
1.0	.4870	.4158	.2907	.1122
1.1	.5107	...	.3018	.1079

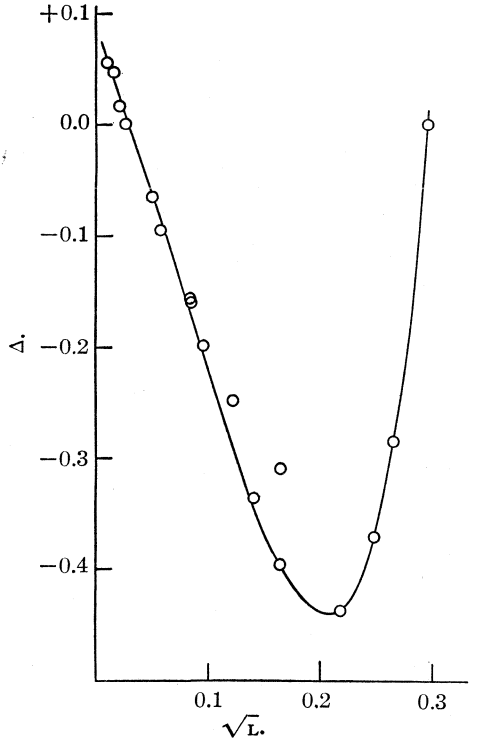


Fig. 1.—Conductance curve for potassium nitrate. $\Delta = (M/L) - 9.401 - 24.341\sqrt{L}$.

The smoothed values were obtained from deviation curves made by the methods described in the first paper.[2] Figures 1 and 2 give illustrative small-scale reproductions of the conductance and freezing point curves for potassium nitrate. The broken line in the latter shows the deviation from the zero line corresponding to two hundred-thousandths of a degree. The crosses give the measurements of Adams.[3] The curves extrapolate naturally to a horizontal tangent at zero concentration, that is, to the theoretical limiting law, but the measurements in very dilute solutions are not accurate enough to preclude a change of a few per cent. in the limiting law.

Table III gives at round concentrations the values of j determined from the smooth curves,

[3] Adams, THIS JOURNAL, **37**, 481 (1915).

and Table IV the values of γ' calculated from the same curves as described in the previous paper.[2] Both tables give values according to the theoretical limiting law; in no case do we obtain a larger effect. For potassium nitrate the effect is never much smaller even at the highest concentrations. For lithium nitrate, on the other hand, j becomes negative in concentrated solutions.

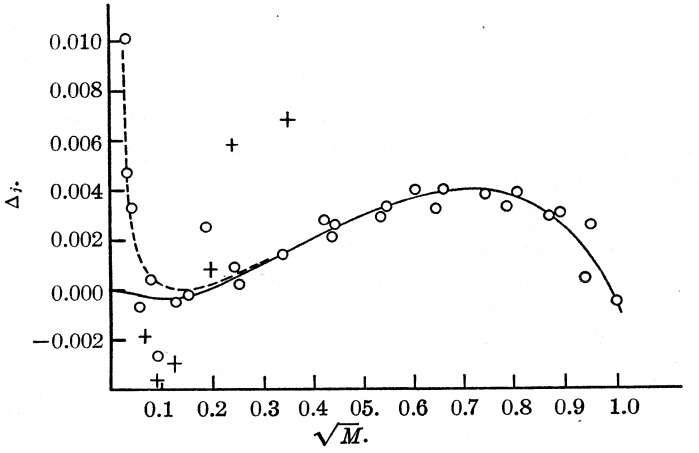


Fig. 2.—Δ_j Values for KNO_3; $\Delta_j = j - \frac{0.3738\sqrt{M}}{1+\sqrt{M}} - 0.1245\,M$.
○, our results; +, Adams' results. Broken line represents the deviations for 0.00002°.

The large effects for potassium nitrate have often been attributed to the smallness of the nitrate ion, or to the charge lying near the surface.[4] The fact that sodium nitrate and lithium nitrate have so much smaller effects is enough to make this explanation highly improbable. From the point of view recently published by one of us,[1] the explanation for the difference between the nitrate and the bromide or iodide ions should lie either in a larger effect of non-ionic forces or in a smaller decrease of the dielectric constant. For the unsymmetrical nitrate ion we should expect both effects to be smaller, in which case the second effect must predominate. Uncertainty concerning the non-ionic forces in solutions containing an unsymmetrical ion make it desirable to leave further theoretical discussion until more salts have been studied. We shall limit ourselves to the fact that our measurements are quantitatively consistent with a size for the nitrate ion which should be expected from the volume of its solutions and from its salting out effects, a size between those of the bromide and iodide ions.

CAMBRIDGE, MASSACHUSETTS

[4] N. Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, VII, No. 9 (1926); H. Müller, *Physik. Z.*, **28**, 324 (1927); **29**, 78 (1928); Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 289]

THE FREEZING POINTS OF AQUEOUS SOLUTIONS. III. AMMONIUM CHLORIDE, BROMIDE, IODIDE, NITRATE AND SULFATE

BY GEORGE SCATCHARD AND S. S. PRENTISS

RECEIVED MARCH 2, 1932 PUBLISHED JULY 6, 1932

Another common and interesting ion whose dilute solutions can be studied only by freezing point determinations is the ammonium ion. Since accurate measurements are not available, we have determined the freezing points of ammonium chloride, bromide, iodide, nitrate and sulfate by the method previously described.[1]

It might appear that the hydrolysis of ammonium salts should make the interpretation of the measurements complicated. A simple calculation will show, however, that the effect of hydrolysis is well within the experimental error of the freezing point measurements. Given the reaction $NH_4^+ \rightleftarrows NH_3 + H^+$: at 0°, $K = (NH_3)(H^+)/(NH_4^+) = 10^{-10}$, we can consider that in the hydrolysis H^+ replaces NH_4^+, so that the net effect is the addition of one ammonia molecule. Since there is no change in the ionic concentration, we may expect the law of mass action to hold well in terms of concentrations, and we can determine the effect on the freezing point accurately enough by assuming ideal solutions. The total number of ions present, neglecting hydrolysis, is twice the number of ammonium ions, so that the fractional increase in the freezing point depression, p, is

$$p = (NH_3)/2(NH_4^+) = 0.5\sqrt{K/(NH_4^+)} = 0.5 \times 10^{-5}/\sqrt{M}$$

When $M = 0.001$, $p = 16 \times 10^{-5}$ or 0.016%, and it decreases for larger values of M, so it must always be negligible in the range of experimental measurements.

All salts were manufacturer's C. P. or reagent products. The chloride and bromide were recrystallized three times from doubly distilled water; the sulfate was crystallized only twice on account of its great solubility; for the same reason and because of their instability, the iodide and nitrate were not crystallized. The iodide solution was reduced with aluminum amalgam immediately before use. The concentrations of the halide stock solutions were determined gravimetrically as the silver halides; that of the sulfate, gravimetrically as barium sulfate; that of the nitrate was determined by distilling from potassium hydroxide into excess dilute hydrochloric acid and titrating with methyl orange as indicator.[2] The

[1] Scatchard, Jones and Prentiss, Paper I, THIS JOURNAL, 54, 2676 (1932).

[2] Dr. P. T. Jones very kindly carried out the determination of the ammonium nitrate concentration.

mean deviation from the average was less than 0.05% for the halides and 0.1% for the sulfate and nitrate. For the chloride and iodide two stock solutions were prepared and analyzed, with excellent agreement between the two series of conductance measurements.

The conductance results are given in Table I and the freezing point results in Table II. The significance of the various symbols is the same

TABLE I

CONDUCTANCE AT 10°

M	*M/L*	Diff.	*M*	*M/L*	Diff.
		NH_4Cl			
1.3862	12.972	0.000	0.26465	11.471	+0.001
1.2248	12.819	− .004	.14995	11.085	.000
1.2149	12.819	+ .004	.087620	10.763	.000
1.0818	12.682	− .004	.044237	10.418	+ .001
0.83112	12.413	− .003	.044237	10.417	− .001
.79033	12.368	+ .001	.016149	10.031	.000
.65609	12.193	− .004	.007223	9.808	− .001
.51495	11.994	+ .005	.004805	9.731	.000
.47401	11.919	− .002	.001613	9.569	− .004
.33232	11.636	− .004	.000577	9.490	+ .004
		NH_4Br			
1.18095	12.277	0.000	0.034615	10.125	0.000
0.85534	11.996	.000	.017078	9.877	+ .002
.55746	11.672	.000	.015518	9.841	− .004
.34386	11.343	.000	.009230	9.700	− .003
.20916	11.029	.000	.005761	9.597	+ .002
.16130	10.876	+ .002	.002230	9.404	− .002
.13354	10.766	.000	.001272	9.305	.000
.10199	10.613	− .007	.000608	9.147	.000
.064574	10.396	+ .002			
		NH_4I			
1.8840	12.695	+0.002	0.057943	10.388	+0.012
1.8213	12.649	.000	.044088	10.258	.000
1.4685	12.389	− .002	.044088	10.256	− .002
1.2830	12.251	.000	.034590	10.171	+ .009
1.1171	12.122	− .001	.017559	9.928	.000
0.79561	11.853	.000	.016613	9.928	+ .016
.68876	11.754	+ .007	.013512	9.860	+ .008
.59485	11.646	.000	.007631	9.718	+ .009
.45559	11.478	.000	.005491	9.642	.000
.37657	11.363	.000	.004682	9.634	+ .021
.25613	11.131	.000	.003757	9.578	.000
.19048	10.966	+ .004	.001907	9.485	+ .002
.12038	10.718	.000	.001691	9.470	.000
.096743	10.607	− .003	.000940	9.414	.000
.096743	10.608	− .002	.000568	9.376	− .001
.081154	10.528	+ .001	.000511	9.371	+ .001

TABLE I (*Concluded*)

M	*M/L*	Diff.	*M*	*M/L*	Diff.
		NH_4NO_3			
1.4366	14.702	+0.003	0.22780	11.981	−0.001
1.2607	14.388	− .006	.16834	11.712	+ .003
1.0900	14.090	+ .004	.099830	11.295	.000
0.81836	13.603	+ .043	.057259	10.929	− .001
.71732	13.355	+ .001	.042952	10.770	.000
.59504	13.080	− .002	.013872	10.280	− .002
.52595	12.921	+ .006	.007556	10.106	+ .002
.36832	12.480	+ .034	.003233	9.921	− .005
.32255	12.334	− .001	.001572	9.822	+ .001
.31691	12.342	+ .027	.001207	9.792	.000
			.000579	9.726	.000
		$(NH_4)_2SO_4$			
1.2275	10.944	0.000	0.072118	6.891	+0.001
0.96710	10.292	.000	.043974	6.497	− .003
.82328	9.931	.000	.043974	6.502	+ .002
.78876	9.841	− .001	.021918	6.031	.000
.69009	9.580	.000	.011150	5.665	+ .001
.51041	9.072	.000	.006346	5.425	− .001
.31321	8.395	.000	.003447	5.223	− .002
.22160	7.987	.000	.001103	4.970	− .001
.21002	7.926	.000	.000816	4.925	+ .002
.15318	7.593	+ .001	.000310	4.811	.000
.10412	7.216	.000			

TABLE II

FREEZING POINTS

M		Diff.[a]	*M*	*j*	Diff.
		NH_4Cl, Series A			
0.001051	0.0245	+0.0104	0.080360	0.0744	+0.0001
.002771	.0230	− .0011	.11392	.0812	− .0001
.007949	.0379	− .0003	.15844	.0877	− .0004
.019383	.0513	+ .0015	.19550	.0920	− .0002
.041279	.0610	− .0006			
		Series B			
0.001966	0.0199	0.0000	0.069680	0.0718	+0.0003
.006021	.0350	+ .0005	.12968	.0841	+ .0001
.010358	.0411	− .0005	.19792	.0913	− .0012
.029738	.0560	.0000	.25536	.0973	.0000
.052182	.0656	− .0004			
		Series C			
1.0927	0.1106	−0.0011	0.46011	0.1062	−0.0006
0.97093	.1109	− .0011	.36611	.1041	+ .0006
.86311	.1115	− .0002	.26877	.0985	+ .0003
.72116	.1106	− .0004	.19818	.0928	− .0003
.59368	.1096	+ .0001			

TABLE II (*Continued*)

M	*j*	Diff.[a]	*M*	*j*	Diff.
		Series D			
1.1579	0.1117	+0.0001	0.37550	0.1039	0.0000
1.0305	.1122	+ .0003	.27770	.0993	+ .0004
0.80055	.1117	+ .0002	.22171	.0952	+ .0005
.55777	.1083	− .0007	.17424	.0914	+ .0015
		Series E			
1.0891	0.1128	+0.0010	0.59181	0.1101	+0.0006
0.96328	.1132	+ .0012	.23783	.0973	+ .0013
		NH_4Br, Series A			
0.001891	0.0195	−0.0044	0.50718	0.1038	+0.0001
1.1041	.1063	− .0010	.41374	.1018	+ .0003
0.92787	.1072	− .0002	.32062	.0978	− .0002
.76415	.1066	− .0001	.24996	.0941	− .0002
.61896	.1054	.0000			
		Series B			
1.1538	0.1077	+0.0007	0.44897	0.1024	0.0000
1.0124	.1075	.0000	.34970	.0995	+ .0002
0.86818	.1075	+ .0003	.27229	.0956	.0000
.70411	.1066	+ .0003	.21457	.0917	.0000
.57637	.1047	− .0001			
		Series C			
0.001006	0.0103	−0.0054	0.070111	0.0721	0.0000
.001888	.0251	+ .0013	.12805	.0828	.0000
.005694	.0373	+ .0008	.18896	.0902	+ .0006
.014531	.0477	.0000	.27362	.0961	+ .0005
.032780	.0591	− .0002			
		Series D			
0.001416	0.0251	+0.0048	0.053369	0.0672	0.0000
.004199	.0336	+ .0005	.091455	.0767	.0000
.009026	.0415	− .0003	.16898	.0878	+ .0001
.024482	.0559	+ .0010	.22831	.0928	.0000
		NH_4I, Series A			
0.001263	−0.0121		0.065404	0.0650	+0.0003
.002345	+ .0223	+0.0017	.11185	.0736	− .0002
.006267	.0347	+ .0038	.14664	.0780	− .0004
.018523	.0456	+ .0031	.20513	.0845	+ .0003
.044658	.0592	+ .0008			
		Series B			
1.0820	0.1037	+0.0001	0.41264	0.0955	+0.0003
0.95324	.1033	+ .0003	.32475	.0923	+ .0005
.78434	.1011	− .0004	.23455	.0868	+ .0002
.63379	.0999	.0000	.18623	.0828	+ .0003
.52319	.0981	+ .0001			

TABLE II (*Continued*)

M		Diff.[a]	*M*	*j*	Diff.
		Series C			
1.2945	0.1030	0.0000	0.42801	0.0952	−0.0005
1.0088	.1030	− .0002	.33385	.0916	− .0006
0.81930	.1015	− .0005	.26191	.0876	− .0008
.67123	.0998	− .0006	.20560	.0836	− .0007
.54718	.0975	− .0010			
		Series D			
0.000941	0.0252	+0.0121	0.021759	0.0460	−0.0014
.002196	.0270	+ .0069	.055823	.0616	− .0005
.006556	.0309	− .0004	.10930	.0733	.0000
		Series E			
0.001297	0.0248	+0.0091	0.094443	0.0708	0.0000
.003990	.0261	+ .0003	.14688	.0784	.0000
.012196	.0369	− .0024	.22405	.0867	+ .0009
.050610	.0614	+ .0009	.29927	.0913	+ .0008
		NH_4NO_3, Series A			
0.000556	0.0126	+0.0013	0.083174	0.0840	−0.0011
.002942	.0231	− .0011	.14726	.1040	+ .0001
.011487	.0411	− .0009	.27633	.1293	− .0002
.042705	.0676	.0000			
		Series B			
0.001743	0.0223	+0.0030	0.11225	0.0945	0.0000
.007521	.0400	+ .0044	.19919	.1140	− .0014
.024933	.0545	− .0013	.42305	.1507	− .0002
.061835	.0777	+ .0008			
		Series C			
1.7415	0.2667	0.0000	0.75830	0.1880	−0.0002
1.4035	.2421	− .0007	.61929	.1739	− .0001
1.1402	.2221	− .0001	.48804	.1591	.0000
0.92408	.2034	− .0002	.32437	.1372	+ .0001
		Series D			
1.2458	0.2310	+0.0002	0.54145	0.1657	+0.0002
1.0050	.2109	+ .0001	.37427	.1446	+ .0003
0.83275	.1954	+ .0001	.24326	.1239	+ .0001
.68833	.1811	.0000			
		Series E			
0.001517	0.0172	−0.0010	0.007547	0.0369	+0.0012
.004245	.0294	+ .0012			
		$(NH_4)_2SO_4$, Series A			
0.000906	0.0412	−0.0028	0.052704	0.2031	+0.0006
.001764	.0633	− .0026	.10874	.2442	+ .0002
.004028	.0923	+ .0019	.16013	.2684	+ .0004
.009905	.1275	+ .0050	.21769	.2880	.0000
.023563	.1676	+ .0066			

TABLE II (*Concluded*)

M	*j*	Diff.[a]	*M*	*j*	Diff.
		Series B			
0.001412	0.0572	0.0000	0.040621	0.1882	−0.0004
.002631	.0781	+ .0009	.088704	.2323	+ .0004
.008660	.1169	.0000	.16811	.2711	.0000
.014973	.1378	− .0019	.28660	.3069	+ .0003
		Series C			
1.2141	0.4060	0.0000	0.49970	0.3458	0.0000
0.92493	.3877	− .0017	.38804	.3278	+ .0001
.75577	.3755	− .0001	.30218	.3099	− .0003
.61168	.3603	.0000	.23352	.2927	.0000
		Series D			
1.0335	0.3964	0.0000	0.33982	0.3183	0.0000
0.83054	.3822	.0000	.26711	.3017	.0000
.68289	.3684	.0000	.19208	.2797	− .0001
.55992	.3535	− .0004	.13237	.2567	+ .0006
.43868	.3363	− .0001			
		Series E			
0.002635	0.0795	+0.0021	0.043134	0.1926	+0.0009
.005001	.0974	.0000	.072053	.2193	− .0005
.012175	.1307	− .0001	.099183	.2383	− .0002
.025376	.1652	+ .0007			

[a] For concentrations below 0.01 *M* the temperatures, in hundred thousandths of a degree, corresponding to the *j* differences are in order: NH_4Cl, A, 4, 1, 2; B, 0, 1; NH_4Br, A, 3; C, 2, 1, 2; D, 2, 1; NH_4I, A, 10, 1, 8; D, 4, 5, 1; E, 4, 0; NH_4NO_3, A, 0, 1; B, 2, 12; E, 1, 1, 3; $(NH_4)_2SO_4$, A, 1, 2, 4, 24; B, 0, 1, 0; E, 3, 0.

TABLE III

j VALUES OF THE AMMONIUM HALIDES AND NITRATE

M	Lim. law	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3
0.001	0.0118	0.0140	0.0161	0.0135	0.0150
.002	.0167	.0203	.0243	.0192	.0205
.005	.0264	.0321	.0349	.0282	.0302
.01	.0374	.0411	.0431	.0367	.0398
.02	.0529	.0503	.0520	.0461	.0517
.05	.0836	.0652	.0663	.0604	.0714
.1	.1182	.0787	.0784	.0718	.0908
.2	.1672	.0927	.0906	.0839	.1156
.3	.2047	.1003	.0971	.0905	.1334
.4	.2364	.1048	.1010	.0948	.1479
.5	.2643	.1078	.1035	.0975	.1606
.6	.2897	.1097	.1052	.0994	.1720
.7	.3127	.1108	.1063	.1006	.1824
.8	.3343	.1116	.1070	.1017	.1922
.9	.3546	.1118	.1073	.1025	.2015
1.0	.3738	.1119	.1074	.1032	.2104
1.1	.3920	.1116	.1072	.1036	.2189

as in the preceding paper.[3] For the halides Table III gives the j values determined from the smooth curve at round concentrations, and Table IV gives the values of γ' determined from the same curves. Table V gives the same data for ammonium sulfate. The limiting laws are given in all cases.

TABLE IV

VALUES FOR $-\text{LOG } \gamma'$ FOR THE AMMONIUM HALIDES AND NITRATE

M	Lim. law	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3
0.001	0.0154	0.0173	0.0159	0.0169	0.0181
.002	.0218	.0251	.0288	.0242	.0259
.005	.0344	.0405	.0451	.0375	.0401
.01	.0487	.0555	.0605	.0509	.0547
.02	.0689	.0732	.0786	.0674	.0736
.05	.1089	.1025	.1082	.0947	.1064
.1	.1540	.1298	.1351	.1193	.1390
.2	.2178	.1616	.1657	.1479	.1806
.3	.2667	.1818	.1849	.1659	.2101
.4	.3080	.1964	.1988	.1793	.2338
.5	.3444	.2081	.2097	.1897	.2542
.6	.3775	.2172	.2186	.1982	.2722
.7	.4074	.2249	.2260	.2052	.2884
.8	.4356	.2316	.2324	.2114	.3034
.9	.4620	.2373	.2379	.2168	.3174
1.0	.4870	.2423	.2427	.2218	.3306
1.1	.5107	.2466	.2469	.2261	.3431

TABLE V

j AND $-\text{LOG } \gamma'$ VALUES FOR AMMONIUM SULFATE

M	j		$-\log \gamma'$	
	Lim. law	$(NH_4)_2SO_4$	Lim. law	$(NH_4)_2SO_4$
0.001	0.0409	0.0471	0.0533	0.0587
.002	.0579	.0689	.0754	.0856
.005	.0916	.0972	.1193	.1308
.01	.1295	.1228	.1687	.1749
.02	.1831	.1530	.2386	.2294
.05	.2895	.1996	.3772	.3194
.1	.4095	.2390	.5335	.4023
.2	.5791	.2824	.7545	.4994
.3	.7092	.3097	.9240	.5633
.4	.8190	.3298	1.0671	.6118
.5	.9156	.3458	1.1929	.6514
.6		.3590		.6851
.7		.3701		.7141
.8		.3796		.7399
.9		.3876		.7629
1.0		.3944		.7836
1.1		.4001		.8025

[3] Scatchard, Prentiss and Jones, Paper II, THIS JOURNAL, **54**, 2690 (1932).

With the ammonium salts there is no question of j approaching the limiting law asymptotically within the range of experimental measurements. The curves all cross the limiting law between 0.005 and 0.02 M. This is illustrated in Fig. 1 by the deviation curve for ammonium bromide, in which the theoretical limiting law is drawn in as a broken line. The existence of this "hump" makes the extrapolation to zero concentration difficult. Since we consider that there is enough evidence from other salts of the general accuracy of the Debye–Hückel limiting law, we have used it, and we have made use of the plot of $j/\sqrt{M}$ to aid in the extrapolation.[4]

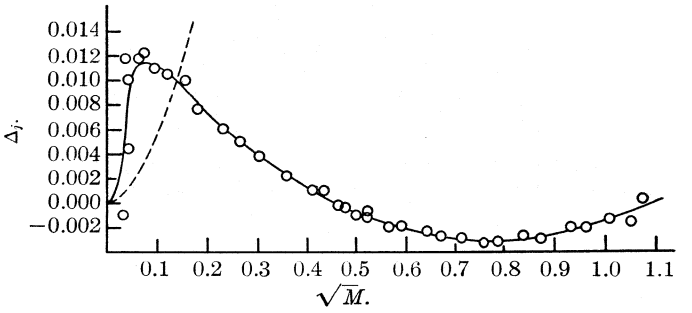


Fig. 1.— Δ_j Values for NH_4Br: $\Delta_j = j - \frac{0.3738\sqrt{M}}{1 + 1.6\sqrt{M}} + 0.0349\,M$.
Broken line represents the limiting law.

This uncertainty of extrapolation makes no difference of course in the j values in the region where the curve is fixed by the experimental measurements, and would make no difference in the values of γ' if the standard state were chosen in this same region. Since we have chosen zero concentration as the standard state, however, any change in the extrapolation will add the same quantity to each value of log γ', in the region where j is unchanged.

We know of no other uni-univalent salts which show evidence of j values larger than those of the Debye–Hückel limiting law and have therefore searched carefully for some other explanation of our measurements. We have already shown that the effect of hydrolysis would decrease j rather than increase it, and that it is much smaller than the measured increase. If the ammonia formed by hydrolysis were carried away by the stream of nitrogen, the net result would be the replacement of some ammonium salt by the equivalent amount of the corresponding acid. This would not change the freezing point measurement appreciably but would give a much higher conductance and apparent concentration, and so too large a value of j. Although calculations indicated that such an effect must be of a much smaller magnitude than the measured effect, we decided

[4] Randall and White, THIS JOURNAL, **48**, 2514 (1926).

to test it experimentally. A stream of nitrogen was passed through ammonium bromide solution at 0° after passing through potassium bromide solution of about the same concentration. The rate was the same as the rapid flow during the freezing point measurements; the time was 160 minutes, or five times that in a regular run. The initial conductance corresponded to a concentration of 0.017979 M, the final to 0.017976 M. The change was -0.017%, again much too small and in the wrong direction to account for our results. An error of more than 1% in analyses that agree to better than 0.1% seems out of the question, and we can find no other reasons to doubt the accuracy of our measurements.

The measurements with ammonium iodide are less accurate because of the instability of this salt. The data definitely indicate a smaller "hump" than for the bromide, and we believe that our extrapolation with a much smaller "hump" best represents the measurements.

Fajans and Karagunis[5] have noted that the freezing point curves for the alkali halides all belong to a consistent family in the sense that no curve appears to cross any other. On the other hand, the curves for ammonium chloride and bromide cross each other and each appears to cross the curve of the corresponding potassium salt, and presumably those of the rubidium and cesium salts. It must be admitted, however, that only for potassium chloride have we accurate enough measurements to be sure that there is not a "hump" of the same order of magnitude as for the ammonium salts. For the nitrate the evidence is much better because we have for comparison our measurements on the alkali nitrate made in the same apparatus. We have already noted that we obtained in no case a j value larger than the limiting law. Our measurements should be accurate enough to ensure that our curves do not cross the limiting law above 0.005 M. For ammonium nitrate, on the other hand, the curve crosses the limiting law between 0.01 and 0.02 M and shows a hump about the same size as that of ammonium chloride. The ammonium and potassium nitrate curves also cross each other at about 0.04 M.

There seems little doubt that there is some factor operative with the ammonium salts which is negligible with other uni-univalent salts. Its effect is similar to that of association, which proves only that it is operative only when the ions are close together, except that it is swamped out surprisingly soon by the factors which tend to increase the activity coefficient. We do not believe that it should be attributed to a small value of the "collision diameter," a,[6] because the value demanded would be improbably small, and smaller for the bromide than for the chloride. For the uni-

[5] Fajans and Karagunis, *Z. Elektrochem.*, **43**, 1046 (1930).

[6] N. Bjerrum, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, VII, No. 9 (1926); H. Müller, *Physik. Z.*, **28**, 324 (1927); **29**, 78 (1928); Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

bivalent sulfate a small collision diameter might explain part of the effect, but there is no reason to suppose that the factor which affects the halides is not also operative here. We are unable to say what this factor is.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE SPECIFIC HEATS OF FIVE ORGANIC LIQUIDS FROM THEIR ADIABATIC TEMPERATURE–PRESSURE COEFFICIENTS

BY WILLIAM T. RICHARDS AND JOHN H. WALLACE, JR.

RECEIVED MARCH 5, 1932 PUBLISHED JULY 6, 1932

Introduction

Although the specific heats of liquids have been measured for nearly two centuries, there remains a distressing lack of agreement in the immense collection of numbers which have been reported to represent them. Because of the complexity of the correction factors which must be applied to the results of calorimetric determinations, it is not uncommon to find a divergence of ten per cent. between two investigations, although the estimated error of each is far below this value. While it is not at present possible to interpret the specific heats of most liquids even to this approximation, accurate knowledge of so fundamental a property must be ultimately both necessary and valuable. Any method other than the calorimetric should, therefore, be considered if it appears to offer a practical alternative.

From the first and second laws of thermodynamics, without further assumption, it follows that the adiabatic temperature–pressure coefficient of a system of heat capacity at constant pressure C_p is given by the expression

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p$$

where T, p, s and v represent temperature, pressure, entropy and volume, respectively. Oersted[1] appears to have been the first to sense this relationship qualitatively, for he subjected water to a sudden pressure and attempted to measure a rise in its temperature. The formal derivation was carried out by Joule,[2] who experimentally proved the second law of thermodynamics by measuring the heat capacity, coefficient of thermal expansion and temperature–pressure coefficient of water and of fish oil. Several other investigations have subsequently dealt with the last of these quantities for solids, liquids and gases, although the majority do not lend themselves even to approximate calculation of specific heats, owing to the magnitude of the pressures employed. Creelman and Crocket,[3]

[1] Oersted, *Ann. chim. phys.*, **2**, 22, 192 (1823).

[2] Joule, *Phil. Mag.*, **17**, 364 (1859).

[3] Creelman and Crocket, *Proc. Roy. Soc. Edinburgh*, **13**, 311 (1885).

Burton and Marshall,[4] and Pushkin and Grebenschikov,[5] for example, examined several liquids in this way, but used pressures always in excess of 300 atmospheres. Barus[6] calculated the specific heat of water from interferometric data using the relationship derived by Joule. Finally, Dixon and Rodebush,[7] following the republication of the equation by Lewis and Randall,[8] used it to obtain the heat capacities of several liquid metals, and showed that an accuracy of 2% was attainable. Although it has several times been suggested that experiments of this kind are suitable for the determination of the specific heats of organic liquids, no searching test of the method appears hitherto to have been undertaken.

Experimental Method

It follows from the equation above that measurements of temperature and pressure suffice, if made under securely adiabatic conditions, to determine without correction the specific heat of a liquid, provided that its coefficient of thermal expansion is known. This may safely be taken from the literature, as it is by far the most readily measured of the various characteristic coefficients.

Of the several types of apparatus which suggest themselves for such an investigation the simplest was chosen. This consisted of a Geneva Society pump which was connected by means of a suitable valve system to a Bourdon type gage and to a pressure bomb of conventional design. The system was filled with castor oil, the connections and valves being of 1 cm. internal diameter to secure a rapid response to changes in pressure. The bomb contained a cell of the construction illustrated in Fig. 1. The wires from the copper–constantan thermoelement in the cell were passed out of the bomb through a hard rubber plug and suitable insulating tubing, leaks being effectively prevented by tightening the plug around the wires with a metal collar and gland nut. The other junction of the thermoelement system was immersed in a Dewar flask in the thermostat which contained the pressure bomb. Thus a zero potential difference was secured at the start of each measurement. The change of temperature following a change of pressure was ascertained by calibration of the thermoelement system. A White double potentiometer, one branch of which was connected to a control pair thermocouples outside the bath to indicate stray currents in the electrical system, was used to measure the change of potential corresponding to a given temperature difference. The standard practice with respect to shielding, insulation and prevention of stray currents due to bimetallic junctions in the circuit or motion of wires in the earth's magnetic field was observed. The precision of the results will be discussed below.

After calibrating the thermoelements and filling the cell with a suitable liquid, measurements were obtained by a uniform procedure. A difference of pressure was first established and, after temperature equilibrium had been reached, the reading of the gage was recorded, and the absence of stray currents in the galvanometer circuit con-

[4] Burton and Marshall, *Proc. Roy. Soc.* (London), **50,** 130 (1891).

[5] Pushkin and Grebenschikov, *J. Chem. Soc.*, **123,** 2717 (1923); **125,** 2043 (1924).

[6] Barus, *Pub. Carnegie Inst.*, **249,** 4 (1919).

[7] Dixon and Rodebush, THIS JOURNAL, **49,** 1162 (1927).

[8] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 137.

firmed. An approximate calculation of the temperature drop to be expected from the release of the pressure was then made, and the potentiometer set with the circuit open to balance the corresponding potential difference. The pressure was then reduced to atmospheric by opening a valve, and the galvanometer circuit closed. Any difference between the calculated and the observed deflection was added to the potentiometer setting on the basis of a previous calibration of the galvanometer scale in microvolts per cm., and the result converted into temperature rise in degrees centigrade per bar (or per dyne $\times 10^6$).

Accuracy of Pressure Measurements.—The gage employed was calibrated in divisions of 0.33 atm. to 0.5% accuracy between 15 and 50 atm. The accuracy of the calibration was maintained by frequent checks against an absolute piston gage. The Bourdon gage method of determining pressures, although open to criticism on the ground that it does not permit the highest possible precision, was found both practical and accurate over the necessary range. Gages of several other types were tested and abandoned because of clumsiness, hysteresis or other serious defects.

Temperature.—The absolute temperature of the pressure bomb and the constant temperature side of the thermoelement pair was fixed as desired to $\pm 0.005°$ by a conventional water thermostat. Owing to the thermal inertia of the bomb and its contents, and of the Dewar flask in which the constant temperature junction was fixed, fluctuations about the mean temperature in the bath were imperceptible in the electrical system. The value of the absolute temperature was read from a Bureau of Standards calibrated thermometer to 0.02°.

The difference between the temperature of the liquid before and after a measured change of pressure was a determining factor in the accuracy with which the specific heat could be calculated and was, therefore, given careful attention. Obviously the heat capacity of the junction used must be small enough so that it does not measurably alter the temperature assumed by the liquid after the adiabatic expansion. Also, the thermocouple must reach the temperature of the liquid within a few seconds after the change of pressure in order that the gradual return of the temperature of the liquid to that of the bath shall not measurably lower the observed temperature difference. Finally, since the adiabatic temperature–pressure coefficients of the liquid and of the glass walls into which the thermocouple is sealed are not identical, the length and surface of wire between the walls and the junction must be great enough in relation to the thermal conductivity of the wire to prevent the temperature of the walls from influencing that of the junction.

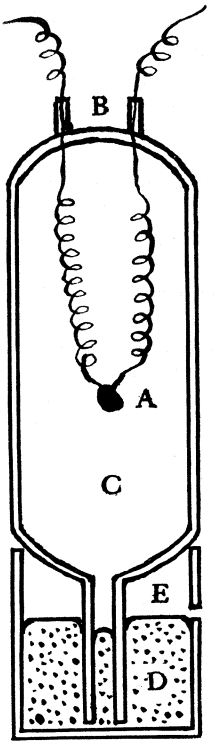


Fig. 1.—Cell for the measurement of the adiabatic temperature–pressure coefficient. The flattened thermoelement A is led out through the glass walls at B. The cell is entirely filled with liquid C, and mercury D employed to transmit the pressure impulse from the castor oil E.

The optimum dimensions for wires and cell are, therefore, difficult if not impossible to calculate. They were ascertained experimentally by photographing the response of the galvanometer to the potential generated by a release of pressure and comparing this to its response to an instantaneous difference of potential of like magnitude. As expected, the two were not comparable if the thermoelement was too coarse, too near the

glass walls, or immersed in too small a volume of liquid. In the experimental arrangement finally adopted and illustrated in Fig. 1, the response of the galvanometer to the release of pressure was as rapid as that to an instantaneous difference of potential, the maximum deflection being reached in both cases at the end of the period (5.4 sec.) of the critically damped galvanometer. The characteristic time–deflection curve before the maximum was almost identical in the two cases. The maximum deflection of the galvanometer persisted without measurable change for more than fifteen seconds after the critical period of the galvanometer had elapsed, showing that the slow return of the liquid to the temperature of the bath did not affect the accuracy of the observed temperature difference within a time interval easily sufficient to make the necessary measurements. This behavior is considered adequate proof that the release of the pressure and the response of the thermocouple were attained within a sufficiently short period, and that, therefore, the maximum deflection represented, except for an extremely slight correction due to work done on the galvanometer, the actual adiabatic temperature change corresponding to a given pressure.

The several thermoelements used were calibrated individually in exactly the temperature range for which they were employed by the usual method of immersing one junction in ice water and the other in a bath at the desired temperature and measuring potentiometrically the resulting difference in potential. All thermoelements used gave concordant potentials under similar conditions, the resulting temperature–potential function being essentially in agreement with that of Adams.[9] The accuracy of the potentiometric system and the Beckmann thermometer employed defined the accuracy of the resulting calibration: the potential could be read to ± 0.05 microvolt, which gave an accuracy of $\pm 0.001°$ to any single observation.

It may, therefore, be stated, to summarize the accuracy of the measurements, that the estimated absolute error of pressure was 0.5%, and of temperature 0.2% in the range used for investigation. It should be pointed out, however, that both pressure and temperature errors were apparently entirely random, and were, therefore, greatly reduced by multiplication of observations.

Purification of Materials

Benzene.—Starting with a guaranteed reagent grade the liquid was washed with sulfuric acid until no further darkening occurred, then repeatedly with dilute sodium hydroxide, and finally with water. It was then twice fractionally crystallized, dried with calcium chloride, and refluxed over phosphorus pentoxide. Finally it was twice fractionated, the second time from sodium wire. For the sample used the corrected b. p. was $80.20 \pm 0.05°$, $n_D^{20°}$ 1.50132.

Toluene.—This was similarly washed with sulfuric acid, sodium hydroxide and water. It was dried with calcium chloride and refluxed with phosphorus pentoxide. Finally it was twice fractionated, the second time from sodium wire. For the sample used corrected b. p. was $110.50 \pm 0.05°$, $n_D^{20°}$ 1.49630.

Carbon Tetrachloride.—A reagent grade was refluxed over mercury, washed with sulfuric acid, sodium hydroxide and water, dried with fused calcium chloride, and twice fractionated from freshly fused calcium chloride. For the sample used the corrected b. p. was $76.50 \pm 0.05°$, $n_D^{20°}$ 1.46032.

Chloroform.—The accepted method of purification was found unsatisfactory for this substance owing to its partial oxidation to phosgene by washing with sulfuric acid, sodium hydroxide and water. Each sample was, therefore, merely fractionated from fresh fused calcium chloride, its boiling range and index of refraction being thus brought within the desired limits. Three samples from widely divergent sources were so pre-

[9] Adams, "International Critical Tables," Vol. I, p. 57.

pared. They had boiling points and indices of refraction, respectively, of 61.15 ± 0.05°, 1.44647; 61.15 ± 0.05°, 1.44607; and 61.20 ± 0.05°, 1.44598. Since no reason to distinguish between them was apparent, the results obtained with them are combined in the tables given below.

Normal Heptane.—This substance was obtained in a high state of purity from the Ethyl Gasoline Corporation. It was dried by fractionating from sodium wire. For the sample used the corrected b. p. was 98.35 ± 0.05°, $n_D^{20°}$ 1.38770.

Numerical Constants.—Since the measurements reported below demonstrate that the quantity $(\partial T/\partial p)_s$ is effectively independent of pressure over a range of 0–30 atm., it follows that C_p is also sensibly constant over this range, and Equation 1 may be written in the form

$$C_p = \frac{\Delta p}{\Delta T}\left(\frac{\partial v}{\partial T}\right)_p \frac{T}{0.4185}$$

where pressure is now in bars, C_p in 15° calories per gram per degree (15° calorie = 4.185 × 10^7 ergs) and T in °K. The values for $(\partial v/\partial T)_p$ were obtained in the extensive form by differentiation of the empirical density–temperature equations given in the "International Critical Tables." This coefficient must not, of course, be confused with the thermal coefficient of expansion, usually designated by α, which is expressed intensively. The volume–temperature differentials were chosen from a single source for the sake of uniformity. If they are subsequently revised a corresponding revision of the calculated specific heat may readily be made.

Typical Determination.—The reproducibility of measurements and

TABLE I

BENZENE 40 °C. $(\partial v/\partial T)_p$ = 146.565 × 10^{-5}. 1 MICROVOLT = 0.02377°

Potential in mv.	ΔT in °C.	Δp in bars	C_P in cal.$_{15°}$
31.10	0.7392	28.61	0.4242
28.52	.6779	26.41	.4271
27.88	.6627	25.72	.4255
27.25	.6477	25.10	.4249
26.63	.6330	24.48	.4240
25.75	.6121	23.79	.4261
25.20	.5990	23.17	.4241
25.15	.5978	23.10	.4237
24.48	.5819	22.55	.4249
24.00	.5705	21.99	.4228
23.20	.5515	21.37	.4251
22.88	.5438	21.17	.4268
22.38	.5320	20.68	.4264
21.63	.5141	20.00	.4264
21.10	.5016	19.37	.4236
20.15	.4790	18.62	.4262
19.70	.4683	18.13	.4246
18.80	.4469	17.31	.4246
18.30	.4350	16.82	.4241
16.95	.4029	15.58	.4241
		Average	.4249

distribution of errors is best illustrated by quoting one series of observations which, in combination with a similar determination with a different thermoelement pair, led to the value for the specific heat of benzene at 40°. The concordance of experimental values was uniform in all determinations, and the results quoted are entirely typical. It will be noted that the temperature–pressure coefficient is sensibly independent of pressure over the observed range. The method is not, however, dependent upon this condition, for a correct value for the specific heat at atmospheric pressure may be obtained by extrapolation if necessary.

Summary of Results

Table II gives in condensed form the results obtained experimentally. Each value for the specific heat is determined by a set of measurements like that quoted in Table I, consisting of from 20 to 30 separate values. The calculated probable error of each value is always far below 0.1%. It has not been recorded, since systematic errors evidently may enter to at least this extent. At least two separate determinations of about twenty observations were made for any particular substance and temperature, always in different cells with different individually calibrated thermoelements.

TABLE II

SUMMARY OF MEASUREMENTS AND CORRESPONDING SPECIFIC HEATS

Temp., °K.	$(\partial T/\partial p)_S$ (av.) deg. atm.$^{-1}$	$(\partial v/\partial T)_p \times 10^3$ from "I. C. T."	Detns.	Average C_P per gram in cal.$_{15°}$
		Benzene		
293.1	0.02396	1.3829	40	0.4095
303.1	.02503	1.4225	45	.4170
313.1	.02617	1.4657	42	.4246
323.1	.02732	1.5127	35	.4332
		Toluene		
293.1	0.02191	1.2370	68	0.4007
303.1	.02272	1.2722	64	.4103
313.1	.02365	1.3125	45	.4201
323.1	.02470	1.3582	44	.4301
		Normal Heptane		
293.1	0.02420	1.8113	49	0.5312
303.1	.02543	1.8661	43	.5383
313.1	.02681	1.9305	50	.5458
		Carbon Tetrachloride		
293.1	0.02677	0.76393	42	0.2022
303.1	.02836	.78746	51	.2038
313.1	.03002	.81314	47	.2053
		Chloroform		
293.1	0.02685	0.85157	62	0.2251
303.1	.02860	.88478	65	.2270
313.1	.03048	.92225	69	.2294

Discussion

The purpose of this investigation was entirely experimental, and no theoretical discussion will be attempted.

It is believed that the determinations quoted above are sufficiently accurate to fix the values of the various specific heats to better than 0.5%. Since no correction factors were necessary and the conditions of the measurements were thermodynamically satisfactory, it is difficult to estimate the systematic error. The agreement of the specific heats obtained with those of previous investigators is on the whole satisfactory, as Table III demonstrates. This is not the place to undertake a detailed analysis of such divergencies as occur.[10]

TABLE III

COMPARISON OF SPECIFIC HEATS WITH THOSE OF PREVIOUS INVESTIGATORS

Benzene

Temp., °C.	R. and W.[a]	H., P. and D.[b]	"I. C. T."[c]	W. and D.[d]	Trehin[e]
20	0.4095	0.4088	0.4062	0.4080	0.4116
30	.4170	.4165	.4146	.4112	.4165
40	.4246		.4229	.4204	.4268
50	.4332		.4330	.4345	.4364

Toluene

	R. and W.[a]	I. C. T.[c]	W. and D.[d]	Trehin[e]
20	0.4007	0.3986	0.3899	0.4126
30	.4103	.4067	.3985	.4243
40	.4201	.4138	.4072	.4361
50	.4301	.4208	.4158	.4459

Normal Heptane

	R. and W.[a]	W. and D.[f]	P., H. and T.[g]
20	0.5312	0.5039	0.5262
30	.5383	.5181	.5325
40	.5458	.5323	

Carbon Tetrachloride

	R. and W.[a]	W. and D.[f]	M. and McR.[h]
20	0.2022	0.1990	0.2016
30	.2038	.2033	.2019
40	.2053	.2047	.2022

Chloroform

	R. and W.[a]	W. and D.[f]	Trehin[e]
20	0.2251	0.2311	0.2276
30	.2270	.2341	.2308
40	.2294	.2372	.2341

[a] Richards and Wallace, this paper. [b] Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930). [c] "International Critical Tables." [d] Williams and Daniels, THIS JOURNAL, **46**, 1569 (1924). [e] Trehin, *Ann. phys.*, [9] **15**, 246 (1921). [f] Williams and Daniels, THIS JOURNAL, **46**, 906 (1924). [g] Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930). [h] Mills and McRae, *J. Phys. Chem.*, **15**, 54 (1911).

[10] A tabulation of all the first thermodynamic coefficients of the liquids here investigated from various sources is being compiled for separate publication by one of us.

Apart from calorimetric determinations, which show too great deviations among themselves to provide adequate comparison without attributing undue importance to a single investigation, only one direct check seems at present possible. The recent results of Shiba on the adiabatic and isothermal compressibilities[11] of benzene, toluene, chloroform, and carbon tetrachloride permit, with a knowledge of the coefficient of expansion, the calculation of the adiabatic temperature–pressure coefficient by the relationship

$$\frac{\left(\frac{\partial v}{\partial P}\right)_S - \left(\frac{\partial v}{\partial P}\right)_T}{\left(\frac{\partial v}{\partial T}\right)_P} = \left(\frac{\partial T}{\partial P}\right)_S$$

TABLE IV

COMPARISON OF THE MEASURED ADIABATIC TEMPERATURE–PRESSURE COEFFICIENT WITH THAT CALCULATED FROM THE RESULTS OF SHIBA

	Benzene			Toluene	
Temp., °C.	25	30	35	25	30
$(dT/dP)_S$ exptl.	0.02449	0.02503	0.02560	0.02231	0.02274
$(dT/dP)_S$ calcd.	.02376	.02431	.02474	.02093	.02112
	Carbon Tetrachloride			Chloroform	
Temp., °C.	25	30		25	30
$(dT/dP)_S$ exptl.	0.02755	0.02836		0.02768	0.02857
$(dT/dP)_S$ calcd.	.02671	.02718		.02672	.02785

Table IV illustrates the agreement between the values calculated by this means and those measured above. It may be seen that the agreement is far from satisfactory. Since the discordance is even greater if the previously accepted values for the specific heat are used to calculate the adiabatic temperature–pressure coefficient, it can hardly be attributed to errors in the measurements here reported. It seems probable, since Shiba's values for the adiabatic compressibility are in fair accord with those calculated from the velocity of sound, that the responsibility for this deviation must be attributed to his isothermal measurements, but the exact reason for it is not apparent from his communication.

Summary

The adiabatic temperature–pressure coefficients for 15 to 30 atmospheres are reported between 20 and 50° for benzene and toluene and between 20 and 40° for carbon tetrachloride, chloroform and *n*-heptane. From these are calculated, using thermal expansion coefficients derived from the "International Critical Tables," the corresponding specific heats. Since the calculated probable errors of these determinations are always below 0.1% and since it is not necessary to apply correction factors to the observed temperature and pressure differences, it is believed that they fix

[11] Shiba, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, **16**, 205 (1931).

the specific heats of the various liquids to better than 0.5%. The specific heats measured by previous investigators, although their mutual discordance makes a comparison difficult, are in fair agreement with those here reported.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

SOLID CADMIUM AMALGAMS. AN X-RAY PROOF OF THE COMPOUND Cd_3Hg

BY NELSON W. TAYLOR

RECEIVED MARCH 7, 1932 PUBLISHED JULY 6, 1932

The possible existence of a compound between cadmium and mercury has been a question of interest for many years. The evidence has been conflicting. If the thermodynamic activity of cadmium is defined as unity for the pure liquid, it is found for liquid cadmium amalgams that the ratio of activity to mole fraction for cadmium is less than unity over the whole concentration range. The same is true of mercury when the activity of pure liquid mercury is taken as unity. Hildebrand, Foster and Beebe[1] found that the vapor pressures of mercury over liquid cadmium amalgams at 323° were less than corresponded to the mole fraction; and Richards and Forbes,[2] who measured concentration cells of cadmium amalgams at room temperature, obtained electromotive force values too large. Both of these criteria indicate an affinity between the two components, which should be manifested in complex or compound formation.[3]

On the other hand, microscopic or thermal analyses of solid alloys of cadmium with mercury have hitherto not brought to light any compound. The constitution diagram, based largely on the work of Bijl and of Mehl and Barrett,[4] shows three solid solutions but no compounds. The stability of any compound which may exist should certainly be greater in the solid than in the liquid state. As the evidence from electromotive force and vapor pressure data is quite trustworthy it was a matter of considerable interest to make an x-ray study of certain amalgam compositions which had not been thoroughly investigated.

R. F. Mehl[5] made x-ray patterns of ten alloys of Cd–Hg and reported that those containing more than 60 weight per cent. (73 atomic per cent.)

[1] Hildebrand, Foster and Beebe, THIS JOURNAL, **42**, 545 (1920).

[2] Richards and Forbes, Carnegie Instit. Pub. No. 56 (1906).

[3] The causes of deviations from ideal solution behavior are given detailed treatment in J. H. Hildebrand, "Solubility," The Chemical Catalog Company, New York, 1924, and in recent journal articles by Professor Hildebrand.

[4] Bijl, *Z. physik. Chem.*, **41**, 641 (1902). Mehl and Barrett, A. I. M. M. E. Tech. Pub. No. 225 (1929).

[5] Mehl, THIS JOURNAL, **50**, 381 (1928).

of cadmium showed an hexagonal close-packed lattice of axial ratio 1.89, while those containing 23 to 50 weight per cent. (64 atomic per cent.) of cadmium were face-centered tetragonal, with axial ratio 0.52. Since McKeehan and Coffi[6] and a number of subsequent workers had shown that pure mercury possessed a rhombohedral lattice, $a = 3.00$, $\alpha = 70°32'$, R. F. Mehl and C. S. Barrett examined the structure of the solid solutions terminal to pure mercury and found that up to 3.5 atomic per cent. of cadmium, the rhombohedral structure persisted. Their work extended the range of face-centered tetragonal solid solutions down to 12 atomic per cent. of cadmium. The range from 3.5 to 12 was two-phase.

Experimental Part

In order to test the possibility of a new crystal phase in the immediate vicinity of a possible compound Cd_3Hg (75 atomic per cent. of cadmium) three alloys were prepared containing 70, 75 and 80.8 atomic per cent. of cadmium, respectively. These alloys were weighed from pure metals, sealed in Pyrex tubes which were then evacuated; they were melted and held as liquids at 285–295° for four hours. They were then cooled quickly to avoid segregation, and the solids tempered at 145 to 149° for twenty-eight hours. The following day filings were made and these filings sealed up and evacuated as before, and tempered at 145–149° for forty-four hours. This treatment avoids oxidation or volatilization and ensures the formation of the most stable crystal phase at the annealing temperature.[7]

Powder x-ray diagrams of these three alloys, each mixed with a small quantity of finely ground sodium chloride were made using a Siegbahn type metal x-ray tube[8] with copper target, and a new type of camera developed by the writer.[9] On account of the rather high absorption coefficient of mercury for CuK radiation about seven hours exposure was required. Mehl, using a larger camera with the more penetrating MoK radiation, required about twenty-four hours for his exposures. A film was also made on filings of pure cadmium mixed with sodium chloride.

The lines on the films forming the sodium chloride pattern were easily identified. Using the known lattice constant $a = 5.628$ Å. for sodium chloride, the true angles of reflection 2θ were calculated[10] from the Bragg equation

$$N\lambda = 2d \sin \theta$$

and a plot was made for each film of observed 2θ versus correction (difference between true and observed 2θ). These calibration curves were then used in getting the correct 2θ values for all the lines due to the alloys

[6] McKeehan and Coffi, *Phys. Rev.*, **19**, 444 (1922).

[7] The alloys were kindly prepared by Dr. B. E. Lauer.

[8] Siegbahn, "Spectroscopy of X-Rays," Oxford University Press, 1925.

[9] Taylor, *Rev. Sci. Instruments*, **2**, 751 (1931).

[10] For a cubic lattice $\sin^2 \theta = (\lambda^2/4a^2)(h^2 + k^2 + l^2)$.

These angles are recorded in subsequent tables together with appropriate calculations. The letters v.w., m, st, signify very weak, medium, strong.

TABLE I

DATA ON PURE CADMIUM (HEXAGONAL)

2θ corrected	$\sin^2\theta$	$\sin^2\theta$ (calcd.)	Index hkl	Intensity
34.50	0.0879	0.0895	100, 010	v.w.
38.50	.1087	.1083	$\bar{1}11$, 101	m
47.85	.1644	.1647	012	w
60.90	.2568	.2588	103	w
62.30	.2676	.2685	110	w
68.70	.3184	.3177	β104	v.w.
71.85	.3438	.3437	112	m
73.10	.3547	.3580	200	w
77.50	.3918	.3905	104	w
81.95	.4300	.4290	β203	v.w.
90.60	.5052	.5097	β210	w
92.95	.5257	.5273	203	m
98.15	.5709	.5697	105	m
104.40	.6243	.6265	210	w
106.70	.6437	.6453	211	m
108.05	.6549	.6590	204	w
113.35	.6982	.7017	212	m

Values of $\sin^2\theta$ (calcd.) for the CuK_α lines are obtained from the quadratic equation for an hexagonal lattice

$$\sin^2\theta = 0.0895\,(h^2 + hk + k^2) + 0.0188\,l^2$$
$$= \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}l^2$$

using $\lambda = 1.539$ Å., $a = 2.97$ Å., $c = 5.61$ Å., $c/a = 1.89$. The good agreement (average deviation = 0.3%) of calculated and observed values of $\sin^2\theta$ shows that these lattice constants a and c are correct within 0.2%.

Since the wave lengths of CuK_α and CuK_β lines are 1.539 and 1.388 Å., the ratio of $\sin^2\theta$ for these two lines reflected from a given plane is $(1.539)^2/(1.388)^2 = 1.229$. The CuK_β lines may be readily identified by use of this constant. Thus for the 104 plane, $0.3905/1.229 = 0.3177$. Observed $\sin^2\theta = 0.3184$.

The values of $\sin^2\theta$ (calcd.) for the CuK_α lines were obtained from the relation

$$\sin^2\theta = 0.0893(h^2 + hk + k^2) + 0.01846(1^2)$$

Setting $\lambda^2/3a^2 = 0.0893$ and $\lambda^2/4c^2 = 0.01846$ gives $a = 2.963 \pm 0.005$ Å., $c = 5.645 \pm 0.008$ Å., $c/a = 1.91$.

It may be seen that the 80.8 atomic per cent. cadmium amalgam has the same hexagonal close-packed structure as pure cadmium, with a slightly greater axial ratio. For the solid solution $c/a = 1.91$, for pure cadmium $c/a = 1.89$. This conclusion checks the results of Mehl, and also of C. v.

Simson,[11] who found the hexagonal structure in an amalgam containing 82 atomic per cent. cadmium.

TABLE II

AMALGAM CONTAINING 80.8% CADMIUM (HEXAGONAL)

2 θ corrected	Sin² θ	Sin² θ (calcd.)	Index *hkl*	Intensity
34.40	0.0874	0.0893	100, 010	w
38.40	.1082	.1079	$\bar{1}11$, 101	m
47.60	.1629	.1631	012	m
54.00	.2061	.2072	β103	w
60.55	.2542	.2551	103	w
62.40	.2684	.2685	110	w
63.45	.2765	.2780	β112	w
65.10	.2895	.2905	β200	v.w.
71.60	.3422	.3421	112	m
73.35	.3567	.3580	200	w
81.50	.4261	.4255	β203	v.w.
82.30	.4330	.4316	202	w
90.60	.5052	.5098	β210	v.w.
95.50	.5479	.5495	105	w
97.20	.5627	.5629	114	m
104.85	.6281	.6266	210	w
107.10	.6470	.6449	211	m
113.40	.6986	.7001	212	m
120.0	.7500	.7519	106	m

The Tetragonal Solid Solution.—An excellent pattern of the face centered tetragonal solid solution is given by C. v. Simson for an amalgam containing 50 atomic per cent. cadmium. She tabulates values of the line position 1 on the film for a camera of radius 2.47 cm. From this one may calculate θ in the Bragg equation $n\lambda = 2d \sin \theta$. Using $\lambda = 1.539$ Å. for

TABLE III

FIFTY ATOMIC PER CENT. CD (F.-C. TETRAGONAL)

l (Simson)	θ	Sin² θ	Sin² θ (calcd.)	Index *hkl*	Intensity
2.78	16°06′	0.0769	0.0767	200	v.st.
3.34	19°22′	.1100	.1095	111	m
3.98	23°05′	.1536	.1534	220	st
4.76	27°37′	.2147	.2139	β131	w
5.32	30°50′	.2626	.2629	131	v.st.
5.67	32°50′	.2940	.2941	β202	w
5.79	33°34′	.3058	.3067	400	st
6.37	36°58′	.3617	.3615	202	m
6.60	38°16′	.3838	.3834	240	st
6.92	40°06′	.4150	.4163	331	st
7.15	41°29′	.4390	.4382	222	m.st.
8.43	48°52′	.5673	.5696	151	st
8.65	50°08′	.5891	.5915	402	m.st.
9.57	55°28′	.6786	.6791	113	m

[11] Simson, *Z. physik. Chem.*, **109**, 197 (1924).

CuK_α, I have computed the corresponding values of $\sin^2\theta$ and listed them together with the indices *hkl*. Table III contains this material.

Values of $\sin^2\theta$ (calcd.) are obtained from the quadratic equation for a tetragonal lattice

$$\sin^2\theta(\text{calcd.}) = 0.01917(h^2 + k^2) + 0.07124\,l^2$$

Setting $\lambda^2/4a^2 = 0.01917$ and $\lambda^2/4c^2 = 0.07124$ give

$$a = 5.558 \pm 0.006\ \text{Å.},\ c = 2.883 \pm 0.003\ \text{Å.},\ c/a = 0.519$$

The agreement between observed and calculated values of $\sin^2\theta$ is satisfactory so that one may have confidence in the lattice constants a and c. Mehl's lattice constants for the tetragonal solid solution are $a = 5.570$ Å., $c = 2.896$ Å., $c/a = 0.520$. These values are based on averages of a number of patterns representing alloys of different composition.

Amalgams Containing 70 and 75% Cadmium. New Structure.—Table IV presents $\sin^2\theta$ values from films No. 93 and No. 92, which were made from the 70 and 75% amalgams, respectively. The fifth column gives the average or in some cases the best value, giving consideration to the intensities of the lines. The last two columns give calculated values of $\sin^2\theta$ and the corresponding indices of the reflecting planes.

TABLE IV

SEVENTY AND SEVENTY-FIVE ATOMIC PER CENT. CADMIUM

Film 93, 70% Cd Intensity	Film 93, 70% Cd $\sin^2\theta$	Film 92, 75% Cd $\sin^2\theta$	Film 92, 75% Cd Intensity	$\sin^2\theta$ Average	$\sin^2\theta$ (calcd.)	Index *hkl*
v.w.	0.0051			0.0051	0.0063	101
w	.0109	0.0109	w	.0109	.0087	200
w	.0182			.0182	.0173	220
		.0322	v.w.	.0322	.0335	222
		.0364	v.w.	.0364	.0347	400
v.w.	.0420			.0420	.0433	420
w.	.0606			.0606	.0595	422
v.w.	.0640			.0640	.0648	004
w	.0688	.0686	m	.0687	.0694	440
		.0826	v.w.	.0826	.0821	224
		.0889	m	.0889	.0867	260
w	.0978	.0992	m	.0985	.0995	404
w	.1101	.1082	m	.1091	.1081	424
w	.1262	.1265	m	.1264	.1289	462
w	.1376	.1382	m	.1379	.1387	800
		.1651	w	.1651	.1636	822
		.1770	w	.1770	.1766	752
		.1894	v.w.	.1894	.1896	842
w	.2047	.2042	m	.2045	.2035	804
v.w.	.2321	.2325	w	.2323	.2330	1002
w	.2388	.2395	w	.2392	.2382	844
		.2463	v.w.	.2463	.2460	952
v.w.	.2492			.2492	.2492	871
		.2550	v.w.	.2550	.2585	646
v.w.	.2607			.2607	.2592	008

TABLE IV (*Concluded*)

Film 93, 70% Cd Intensity	Film 93, 70% Cd $\sin^2\theta$	Film 92, 75% Cd $\sin^2\theta$	Film 92, 75% Cd Intensity	$\sin^2\theta$ Average	$\sin^2\theta$ (calcd.)	Index *hkl*
w	.2674	.2672	w	.2673	.2676	*1042*
		.2744	v.w.	.2744	.2765	228
w	.2808	.2828	v.w.	.2818	.2816	864
v.w.	.2950	.2956	v.w.	.2953	.2948	*1060*
		.3095	v.w.	.3095	.3121	*1200*
		.3200	v.w.	.3200	.3192	846
		.3286	v.w.	.3286	.3286	448
m	.3434	.3424	m	.3429	.3422	884
		.3467	v.w.	.3467	.3468	*1240*
v.w.	.3530			.3530	.3554	*1080*
w	.3601	.3626	v.w.	.3614	.3630	*1242*
					.3628	866, *1006*
		.3841	v.w.	.3841	.3856	*1224*
v.w.	.3918	.3928	v.w.	.3923	.3914	857
v.w.	.4093	.4076	m	.4076	.4064	*1262*
					.4066	828
w	.4144	.4140	m	.4142	.4137	*2010*
					.4131	668
v.w.	.4239	.4235	v.w.	.4237	.4232	886
v.w.	.4356	.4352	w	.4354	.4335	*1420, 10 100*
w	.4625	.4616	w	.4621	.4614	*5110*
					.4608	*1107*
		.4660	v.w.	.4660	.4666	*1226*
		.4778	m	.4778	.4760	868, *1008*
		.4978	w	.4978	.4983	*10104, 1424*
w	.5017			.5017	.5013	*1086*
		.5118	w	.5118	.5106	*1048*
		.5231	w	.5231	.5243	*1444*
w	.5627	.5635	w	.5631	.5636	*1620*
					.5611	*6610*
w	.5791	.5804	m	.5800	.5800	*1228*
					.5798	*1622*
					.5832	*0012*
		.6176	m	.6176	.6179	*4012*
					.6147	*1088*
		.6504	m	.6504	.6494	*1268*
					.6526	*4412*

The agreement between observed and calculated value of $\sin^2\theta$ is satisfactory. For the CuK_α lines, $\sin^2\theta$ (calcd.) $= 0.002168(h^2 + k^2) + 0.00405\,l^2$. The lattice is body-centered tetragonal with the constants $a =$ 16.53 Å. $\pm$ 0.3%, $c = 12.09 \pm 0.3\%$ Å., axial ratio $c/a = 0.732$. Attempts were made to derive a structure with smaller lattice constants but without success. The high order of the reflections may possibly be a factor in giving lines of low intensity.

The patterns of films 92 and 93 are practically identical. The lines on No. 92 (75% Cd) are more intense because of the lower mercury content,

mercury being a very good absorber for CuK radiation. This accounts also for certain very weak lines on film No. 92 not appearing on No. 93 or being too faint to measure accurately. A few lines possibly belong to the hexagonal or tetragonal solid solution lattices (*cf.* Tables II and III) but this is not necessarily the case. They may be merely coincidences. If the period of tempering was not quite long enough, traces of the hexagonal or of the other tetragonal solid phase might persist. However, the great abundance of lines which are not to be ascribed to these structures show that a new crystal phase is present. The range of stability of this structure includes 70 and 75 atomic per cent. cadmium and may be a slightly wider range but does not reach 80.8% (at 147°), for the alloy of this composition annealed at the same temperature (145–149°) as the 70 and 75% alloys shows only an hexagonal pattern. Mehl examined an alloy of 60.1 weight per cent. cadmium (73 atomic per cent. Cd) which had been tempered for 120 hours at 170°. His pattern shows lines of the hexagonal lattice only. The discrepancy between his results and mine may lie in the tempering conditions. Annealing the alloy at the lower temperature would favor compound formation. It is noteworthy that whereas according to Bijl's[12] melting point diagram, a 73 atomic per cent. of cadmium alloy should be inhomogeneous, Mehl found only the pattern of the hexagonal (α) solid solution and no tetragonal (ω). The Bijl diagram is in need of revision in this composition region, especially with regard to solid-solid equilibria.

There are other cases known where certain solid phases do not appear if the annealing temperature is too high. Thus alloys of copper with gold show two compounds, AuCu and $AuCu_3$ if annealed below about 400°, but these phases disappear in fifteen minutes if annealed at 400–420° and quenched in water.[13] A comparison of the lattice constants of the new structure with those of the body-centered tetragonal solid solution (50 atomic per cent. cadmium) is instructive. For the 50% Cd alloy

$$a_1 = 3.932 \text{ Å., Mehl; } a_1 = 3.930, \text{ Simson}$$
$$c_1 = 2.896 \text{ Å., Mehl; } c_1 = 2.883, \text{ Simson}$$
$$c_1/a_1 = 0.74$$

These values are computed from the constants of the face-centered lattice by dividing the length of the a axis by $\sqrt{2}$. For the 70 and 75% Cd alloys

$$a_2 = 16.53 \text{ Å.}$$
$$c_2 = 12.09 \text{ Å.}$$
$$c_2/a_2 = 0.73$$
$$\text{Thus, } a_2/a_1 = 2.97\sqrt{2} \text{ and } c_2/c_1 = 2.96\sqrt{2}$$

Each side of the new unit cell is roughly $3\sqrt{2}$ times that of the smaller unit. The volume of the new cell is $54\sqrt{2}$ larger than that of the smaller

[12] Bijl, Ref. 4.

[13] G. Borelius, C. H. Johannsen and J. O. Linde, *Ann. Physik*, **86**, 291 (1928).

cell. Since the latter contains 2 atoms, the new cell must contain 152 atoms. The observed density for the 75% Cd alloy is 10.12 g. per cc. Taking a mean atomic weight of 134.5, the number of atoms per unit cell is computed to be 150.4 ± 1%. Such a cell containing 152 atoms would have 38 Cd_3Hg in the case of the 75% Cd alloy. The complexity of the atomic arrangement in the cell is probably the reason why long annealing at not too high a temperature is necessary to bring about proper orientation and distribution of the atoms.

Alloy systems furnish other examples of large cells. Thus the γ-structure in Cu–Sn alloys has a lattice constant $a = 17.91$ Å. and contains 416 atoms per unit cell.[14] It is possible that the large complex cell found in the Cd–Hg series is an example of a "superstructure" described by Westgren.

Summary

x-Ray examination of solid cadmium amalgams, which had been annealed *in vacuo* at 147° for seventy-two hours, has demonstrated the existence of a new crystal phase, body-centered tetragonal, with lattice constants $a = 16.53$ Å., $c = 12.09$ Å., axial ratio $c/a = 0.73$. The lattice constants are probably correct to 0.3%. The structure evidently contains 152 atoms or 38 molecules of Cd_3Hg. Its composition range includes 70 and 75 atomic per cent. cadmium, and may be slightly wider. It may be regarded as Cd_3Hg or as a solid solution of Hg in Cd_3Hg. The structure is apparently derived from the ω type of solid solutions which characterize alloys poorer in cadmium (down to 12 atomic per cent.).

Confirmation of the hexagonal close-packed structures of pure cadmium and of an 80.8 atomic per cent. of cadmium amalgam has also been obtained.

The bearing of these results on the thermodynamic behavior of cadmium amalgams has been noted.

MINNEAPOLIS, MINNESOTA

[14] A. Westgren and G. Phragmen, *Z. Metallkunde*, **18**, 279 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A SERIES OF SIMPLE BASIC INDICATORS. I. THE ACIDITY FUNCTIONS OF MIXTURES OF SULFURIC AND PERCHLORIC ACIDS WITH WATER[1]

BY LOUIS P. HAMMETT AND ALDEN J. DEYRUP[2]

RECEIVED MARCH 9, 1932 PUBLISHED JULY 6, 1932

Recent work, especially that of Hantzsch and of Hall and Conant, has demonstrated that we have to deal in ordinary chemical systems with a range of acidity much wider than is comprised in the field of dilute aqueous solutions. It has not however given us any single experimental criterion of acidity or any general method of measuring it. When, for instance, the acidity of a solution is determined by means of a simple basic indicator, the thing measured really is the tendency of the acids present, under the conditions prevailing, to transfer hydrogen ion to a neutral organic molecule, the indicator base, converting it to a positive ion. It has been pointed out[3] that such a measure of acidity is not in general the same as that given by an acid indicator, and that neither is a measure of the theoretical concept of hydrogen ion activity.[4]

The "acidity in terms of a basic indicator" is, nevertheless, a most significant quantity, certainly for the equilibrium in any reaction in which hydrogen ion is added to a neutral molecule, and probably for the interpretation of cases of acid catalysis in which the first step is addition of hydrogen ion to a neutral substrate. We have now given it a definite formulation in terms of an acidity function, H_0, and have developed a series of indicators by means of which this function can be measured for any solution whose acidity lies between that of dilute aqueous solutions and that of 100% sulfuric acid.

The possibility of measuring such an acidity function, of applying it to other properties of a solution than the indicator effects which serve to measure it and of determining the relative basicities of indicators by the "step method" which we have used, all depend upon one fundamental assumption. This is that the relative strength of two bases of the same charge type is independent of the medium in which they are compared. The approximate validity of this rule is evidenced by a number of in-

[1] This article is based upon part of a dissertation submitted by Alden J. Deyrup to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, March, 1932.

[2] Gottsberger Fellow, 1931–1932.

[3] Hammett, THIS JOURNAL, **50**, 2666 (1928).

[4] This conclusion is emphasized by the demonstration by Taylor, *J. Phys. Chem.*, **31**, 1478 (1927), and by Guggenheim, *ibid.*, **33**, 842 (1929); **34**, 1540, 1758 (1930), of the theoretical as well as the practical impossibility of the determination of individual ion activities.

vestigations;[5] we shall discuss its precision later in the light of our own results.

We define a simple basic indicator as a non-ionized or neutral substance capable of adding one hydrogen ion per molecule without any complicating further reactions[6] and in such a way that a color change is determined by the extent of the reaction.[7] We further define the strength of such an indicator or of any other monoacid base by the function

$$pK' = -\log \frac{a_{H^+}a_B}{a_{BH^+}} = -\log \frac{c_{H^+}c_B}{c_{BH^+}} - \log \frac{f_{H^+}f_B}{f_{BH^+}} \qquad (1)$$

where a is activity, c is concentration and f is activity coefficient, and refer activities in all solvents to the same reference standard, a dilute aqueous solution. In such a solution therefore

$$\log \frac{f_{H^+}f_B}{f_{BH^+}} = 0$$

$$\text{and } pK' = -\log \frac{c_{OH_3^+}c_B}{c_{BH^+}}$$

If now we determine the ionization ratios of two such bases B and C in any given solution whatsoever

$$pK'_B - pK'_C = -\log \frac{c_B c_{CH^+}}{c_{BH^+}c_C} - \log \frac{f_B f_{CH^+}}{f_{BH^+}f_C} \qquad (2)$$

The first term on the right is measurable colorimetrically if the bases are indicators; our fundamental assumption is equivalent to the statement that the activity coefficient term is zero and that the activity coefficient ratio f_B/f_{BH^+} in a given solution is the same for all bases. From this determination of the ionization ratios we therefore calculate the relative strengths of the two bases by the equation

$$pK'_B - pK'_C = -\log \frac{c_B c_{CH^+}}{c_{BH^+}c_C} \qquad (3)$$

If we have a series of simple basic indicators covering any range of acidities whatever, we may by a stepwise application of this procedure, using any convenient solutions, obtain the base strength relative to water of the whole series. We can thus determine the basicities of those substances, too weakly basic for direct measurement in dilute aqueous solutions, which we must use for the study of strongly acid solutions.

[5] Goldschmidt and Mathiesen, *Z. physik. Chem.*, **119**, 439 (1926); Pring, *Trans. Faraday Soc.*, **19**, 705 (1924); Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135 (1925); Mizutani, *ibid.*, **116**, 350; **118**, 318, 327 (1925); Ebert, *Ber.*, **58B**, 175 (1925); Hall, THIS JOURNAL, **52**, 5115 (1930); Halford, *ibid.*, **53**, 2939, 2944 (1931); Brönsted, *Ber.*, **61**, 2049 (1928).

[6] A mobile tautomerism of either base or ion is not a complication in this sense. See A. A. Noyes, THIS JOURNAL, **32**, 815 (1910).

[7] In the same way a simple acid indicator may be defined in terms of the addition of one hydrogen ion to a singly charged anion. Other types exist but offer less promise of usefulness.

We define the acidity function H_0 by the equation

$$H_0 = \log \frac{c_B}{c_{BH^+}} + pK'_B \qquad (4)$$

It may be interpreted as a measure of the extent to which a base of zero strength (pK') reacts with hydrogen ion in the solution in question, or of the strength of a base which is half converted to the corresponding ion in that solution. In its equivalent form

$$H_0 = -\log a_{H^+} \frac{f_B}{f_{BH^+}} \qquad (5)$$

the equation shows that the value of H_0 is definite and independent of the particular indicator used to measure it to the extent that our fundamental assumption that the ratio f_B/f_{BH^+} is the same for different bases in a given solution is exact. In dilute aqueous solution H_0 becomes equal to the P_H; in acetic acid it is theoretically equal to the $(P_H)^{HAc}$ of Hall and Conant,[8] but differs by an additive constant from the value actually given by their scale. The quantity $a_{H^+}f_B/f_{BH^+}$ is of the type which Guggenheim[9] has shown to have an operational or physical meaning.

It is clear that there is a whole series of acidity functions, and we propose that they be distinguished by a subscript representing the sign of the base in the conjugate acid–base system[10] used for their determination. Thus in terms of the simple acid indicator whose color change is determined by the reaction

$$A' + H^+ \rightleftharpoons HA$$

the acidity function H_- is determined by the equations

$$H_- = \log \frac{c_{A'}}{c_{HA}} + pK_{HA} \qquad (6)$$

$$pK_{HA} = -\log \frac{a_H + a_{A'}}{a_{HA}} \qquad (7)$$

Similarly the acidity functions H_+ and H_{++} are defined by the extent of the indicator reactions

$$B^+ + H^+ \rightleftharpoons BH^{++}$$
$$\text{and } B^{++} + H^+ \rightleftharpoons BH^{+++}$$

respectively.

The number of substances known to give reversible color changes with strong acids is enormous[11] and it is not difficult to find others. These can be used for the measurement of acidity with changing medium only if it

[8] See the first criterion of selection of a scale of acidity given in the footnote, THIS JOURNAL, **49**, 3059 (1927).

[9] Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929).

[10] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[11] The following papers contain extensive lists of examples: Baeyer and Villiger, *Ber.*, **35**, 1189 (1902); Kaufmann and Beisswenger, *ibid.*, **36**, 561 (1903); Hofmann and Kirmreuther, *ibid.*, **42**, 4856 (1909); Hofmann, Metzler and Lecher, *ibid.*, **43**, 178, 183 (1910); Hofmann, Roth, Höbold and Metzler, *ibid.*, **43**, 2629 (1910); Fischer and Gross, *J. prakt. Chem.*, [2] **84**, 377 (1911).

can be shown that they are simple indicators and only if the ionization type can be established. It cannot be too strongly emphasized that the indiscriminate application to solvent systems in general of substances, even such as are satisfactory indicators in dilute aqueous solution, which change color with acids and bases can only lead to confusion.

Fortunately there is among Hantzsch's many contributions to the study of strongly acid solutions an extensive cryoscopic and conductivity study of sulfuric acid as an electrolytic solvent.[12] His results demonstrate that interionic effects are not of great magnitude, and that the type of ionization of an electrolyte dissolved in sulfuric acid may therefore be determined by freezing point measurements. Our cryoscopic results, which will be published in a separate paper, are in qualitative agreement with his but deviate quantitatively in the sense of indicating even smaller interionic effects than do his.

It follows that any substance which is neutral or slightly basic in water, which has a different color in anhydrous sulfuric acid, and which gives a freezing point depression per mole in the latter medium the same as that of other 1:1 electrolytes and approximately twice that of a non-electrolyte, may safely be considered to act as a simple basic indicator at any acidity between that of water and that of pure sulfuric acid. Such a substance does not owe its indicator properties to the addition of a molecule of acid instead of a hydrogen ion. Nor is its indicator function complicated by the dissociation of a molecule of water, as seems to be the case with triphenylcarbinol,[13] for which the color must have a specific dependence upon the activity of water in the solution being studied. Nor is there the overlapping addition of more than one hydrogen ion, which made the successful interpretation of the indicator properties of crystal violet by Conant and Werner so complex experimentally and theoretically.[13,14]

We have selected the fifteen substances described and numbered in Table I as indicators for the range of acidities under investigation. With all but four the conclusion that they are simple basic indicators in this range rests upon our own cryoscopic measurements, which show that they act as strong 1:1 electrolytes in sulfuric acid. For number 1, *p*-nitraniline, we draw the same conclusion from the freezing point work of Oddo and Scandola.[15] Number 4, *p*-nitrodiphenylamine, which is decomposed by

[12] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); **62**, 626 (1908); **65**, 41 (1909); **68**, 204 (1909); *Ber.*, **55**, 953 (1922); **63B**, 1782 (1930). See also Oddo and Scandola, *Z. physik. Chem.*, **62**, 243 (1908); **66**, 138 (1909); *Gazz. chim. ital.*, **39**, II, 1, 44 (1909); **40**, II, 163 (1910); Oddo and Casalino, *ibid.*, **47**, II, 200, 232 (1917); **48**, I, 17 (1918).

[13] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); Conant and Werner, THIS JOURNAL, **52**, 4436 (1930). Dietz and Hammett, cryoscopic work in formic acid to be published.

[14] Safranine, suggested as an indicator for strongly acid solutions by Frey and Elöd, *Ber.*, **64B**, 2556 (1931), is clearly of the same type.

[15] Oddo and Scandola, *Z. physik. Chem.*, **66**, 138 (1909).

100% sulfuric acid, is stable in less concentrated acid and recoverable from it unchanged upon dilution; in structure and reactions it is similar to other nitraniline derivatives. The benzophenone derivatives, 11 and 12, are apparently sulfonated very rapidly in 100% acid, but are recoverable unchanged from less concentrated sulfuric acid; they are assumed to be 1:1 electrolytes in sulfuric acid because benzophenone itself has been found to be a 1:1 strong electrolyte in that solvent.[16]

TABLE I

PROPERTIES OF INDICATORS

No.	Name	Color[a] Base ion	pK' from H_2SO_4–H_2O mixtures	pK' from $HClO_4$–H_2O mixtures	Formic acid
1	*p*-Nitraniline	y−c	(+1.40)	(+1.40)	....
2	*o*-Nitraniline	y−c	+0.16	+0.10	(+0.13)
3	*p*-Chloro-*o*-nitraniline	y−c	−0.56	− .62	− .64
4	*p*-Nitrodiphenylamine	y−c	−2.09	....	−2.21
5	2,4-Dichloro-6-nitroaniline	y−c	−2.93	−2.89	−3.01
6	*p*-Nitroazobenzene	c−y	−3.06	−3.06	−2.99
7	2,6-Dinitro-4-methylaniline	y−c	−4.03	....	....
8	2,4-Dinitroaniline	y−c	−4.09	−4.14	....
9	N,N-Dimethyl-2,4,6-trinitroaniline	y−c	−4.40	....	....
10	Benzalacetophenone	c−y	−5.32	....	....
11	β-Benzoylnaphthalene	c−y	−5.63	....	....
12	*p*-Benzoyldiphenyl	c−y	−5.90	....	....
13	6-Bromo-2,4-dinitroaniline	y−c	−6.30	....	....
14	Anthraquinone	c−y	−7.86	....	....
15	2,4,6-Trinitroaniline	y−c	−9.0	....	....

[a] This refers to the visual effect at the dilutions used in indicator work. c = colorless, y = yellow.

In the course of this selection we have rejected as unsuitable (in some cases possibly with insufficient study) the following substances which give color changes with strong acids: triphenylcarbinol and its simple derivatives because of the evidence previously cited that they are not simple indicators; dibenzalacetone because Hantzsch[16] found it to give a freezing point depression in sulfuric acid twice that of a 1:1 electrolyte; phenolphthalein, cresolphthalein, thymolphthalein, alizarin, *p*-nitroanisole, nitrofluorene, anisal-cinnamal-acetone, anisalacetophenone, piperonalacetophenone, cinnamalacetophenone, because our own experiments showed them to give greater freezing point depressions in sulfuric acid than do 1:1 electrolytes or because they are evidently decomposed by the acid; the sulfonephthaleins and all other sulfonic acid derivatives because of the improbability of their being simple bases; aminoazobenzene, dimethylaminoazobenzene, benzene-azo-diphenylamine and other amino-azo compounds, polyaminotriphenylmethane dyes, phenanthraquinone, 1-amino-

[16] Oddo and Casalino, *Gazz. chim. ital.*, **47**, II, 232 (1917); Hantzsch, *Ber.*, **55**, 953 (1922).

and 2-aminoanthraquinone, because they have a second ionization step and second color change in the range investigated; xanthone and 2,4,6,2′,4′,6′-hexanitrodiphenylamine, because of low solubility.

In addition to a proper selection of indicators, any precise indicator work with changing medium must consider the fact that the absorption of light by a colored substance in solution depends to some extent upon the medium in which it is dissolved, even in cases where the inert nature of the solvent makes chemical reaction in the ordinary sense very improbable. From the numerous previous investigations[17] of this "medium effect" and our own experiments the following general conclusions may be drawn: (1) that its magnitude is specific with regard to the colored substance and the change of solvent; (2) that it is not directly dependent on the charge of the colored substance, the color intensity of neutral molecules being changed as well as that of ions; (3) that its magnitude has not exceeded a factor of two in any case investigated.

In theory, therefore, we should make colorimetric comparisons in a constant medium; in practice it is more convenient to do this indirectly, making the direct comparison with a solution either in water or in 96% sulfuric acid. For the case of an indicator which is non-ionized and colored in water and colorless at high acidity, we define "the stoichiometric color intensity relative to water," I_w, of a solution A by the equation

$$I_w = \frac{C_w \cdot L_w}{C_a \cdot L_a} \tag{8}$$

where C_a and C_w are the stoichiometric concentrations of indicator in solution A and in water, respectively, and L_a and L_w are the lengths of a column of solution A and of a column of water containing these concentrations of indicator at colorimetric balance.[18]

We define "the specific color intensity of the colored form relative to water," S_w, by the equation

$$S_w = \frac{[B]_w \cdot L_w}{[B]_a \cdot L_a} \tag{9}$$

where $[B]_w$ is the concentration of the colored base in water, $[B]_a$ its concentration in solution A. From these equations and from

$$C_w = [B]_w \text{ since } [BH^+]_w = 0$$
$$\text{and } C_a = [B]_a + [BH^+]_a$$

we obtain

$$\frac{[BH^+]_a}{[B]_a} = \frac{S_w}{I_w} - 1 \tag{10}$$

[17] H. C. Jones and Guy, *Physik. Z.*, **13**, 649 (1912); Hantzsch and Glover, *Ber.*, **39**, 4153 (1906); von Halban and Ebert, *Z. physik. Chem.*, **112**, 321 (1924); Sidgwick, Worboys and Woodward, *Proc. Roy. Soc.* (London), **A129**, 537 (1930); Kolthoff, *J. Phys. Chem.*, **32**, 1820 (1928).

[18] This is an expression of Lambert's law and Beer's law. See von Halban and Siedentopf, *Z. physik. Chem.*, **100**, 208 (1922); von Halban and Ebert, *ibid.*, **112**, 321 (1924).

A determination of the ionization ratio $[BH^+]/[B]$ and the acidity, H_0, in a given solution must be made by determining I_w, and by then decreasing the acidity with as little change in medium properties as possible until the indicator is completely in the non-ionized colored form. Then $[BH^+] = 0$ and $S_w = I_w$.

If the color change is in the reverse sense (base colorless, cation colored) a similar equation and process are used

$$\frac{[BH^+]_a}{[B]_a} = \frac{I_h}{S_h - I_h} \qquad (11)$$

where I_h = stoichiometric color intensity relative to a medium H, for instance 96% sulfuric acid, in which the indicator is completely converted to the colored form, and S_h = specific color intensity of the colored form relative to the medium H.

The present article describes the standardization of the series of indicators by the use of mixtures of water with sulfuric acid and with perchloric acid, together with some corollaries of the incidental determination of the values of the acidity function, H_0, in these mixtures. These are particularly convenient solutions for the intercomparison of indicators by the step method; within the precision which our fundamental assumption allows, the values of basicity thus obtained will hold for other media. A following article shows that the indicator series thus standardized may indeed be successfully used in the investigation of solutions in the anhydrous solvent formic acid.

Materials and Procedure

Sulfuric Acid.—Chemically pure concentrated sulfuric acid was tested for clarity in the colorimeter (several samples had to be rejected because of a faint brownish tint). It was standardized to ±0.1% by titration with recently prepared 0.1 molar sodium hydroxide solution standardized with potassium acid phthalate from the Bureau of Standards. The value thus obtained was found to check with a gravimetric determination by precipitation of barium sulfate within 0.1%. It was kept in a tightly stoppered bottle, and was again standardized when nearly exhausted to make certain that it had not changed.

Commercial C. P. fuming acid could not be used to make up acid of concentrations greater than 96% because of its color. Decolorization with nitric acid or sodium persulfate left traces of oxidizing substances which destroyed the indicators. Colorless samples obtained from one manufacturer also destroyed indicators. We finally distilled sulfur trioxide from 30% fuming acid directly into 96% acid in an all-glass apparatus.

The various concentrations of acid required were made up by direct weighing of concentrated acid and water. Densities used in calculating indicator concentrations were taken from the "International Critical Tables." In the range of composition between 98 and 100% acid, where the acidity changes so rapidly with water content that volumetric analysis is not sufficiently accurate, solutions were prepared by addition of weighed amounts of water to acid of maximum freezing point.

In the range from 97 to 100% acid, the acidity–composition curves were determined both with the acid described above and with a sample purified by distillation in a plati-

num still. The latter was found to contain no detectable amount of platinum and less than 0.0002 molar sulfur dioxide. The curves were congruent within experimental error.

Perchloric Acid.—C. P. 70% acid was standardized against 0.1 molar sodium hydroxide. It was restandardized at the end of the series of experiments to make certain that it had not changed. Dilutions were made in the same way as with sulfuric acid.

Indicators.—These are listed by number from Table I. Except where otherwise noted they were obtained from well-known dealers. Melting points were determined by the capillary-tube method with a thermometer calibrated at the Bureau of Standards, and have been corrected for stem exposure. The tests of purity indicated by the letters A and B are explained later.

1. M. p. 148.9°. 2. Recryst. from alcohol, m. p. 71.7°. 3. Prepared by neutralization of the hydrochloride; recryst. from water, m. p. 116.1°. B. 4. Recryst. from alcohol, m. p. 133°. B. 5. Prepared by chlorination of 4-chloro-2-nitroaniline by the method of Witt;[19] recryst. from alcohol and from acetone, m. p. 101.1°. A and B. 6. Prepared (a) by nitration of azobenzene;[20] recryst. from acetone to constant m. p. 130.8°. (b) From *p*-nitronitrosobenzene and aniline;[21] recryst. from acetone to constant m. p. 129.2°. Tests of purity—equal specific color intensity and congruent intensity curves of a and b. 7. Prepared by nitration of acet-*p*-toluidide and saponification of the acetyl derivative;[22] recryst. from alcohol and from acetone, m. p. 169°. B. 8. Recryst. from acetone and from alcohol, m. p. 180°; A and B. 9. Prepared by interaction of picryl chloride and dimethylamine;[23] recryst. from acetic acid, m. p. 141°. B. 10. Recryst. from alcohol, m. p. 55.5°. A and B. 11. Prepared by H. P. Treffers in this Laboratory by the method of Montagne;[24] recryst. from alcohol, m. p. 82.7°. B. 12. Prepared by H. P. Treffers by the method of Montagne;[25] recryst. from alcohol, m. p. 101.6°. B. 13. Prepared by bromination of 2,4-dinitroaniline;[26] recryst. from acetic acid, m. p. 150.5–152°. B. 14. Recryst. from alcohol. 15. Recryst. from acetic acid.

Procedure.—For the experiments in sulfuric acid–water mixtures, a solution of known concentration of the indicator in 96% acid was placed in a short buret rigidly clamped and a definite number of drops were allowed to fall into a portion of the solution under investigation, and then a definite number into the liquid to be used as reference standard. A similar procedure was used for the perchloric acid series. For both series the composition of the acid–water mixture was corrected for the effect of the added indicator solution.

The solutions, immediately after addition of the indicator, were brought to 25 ± 3°, transferred to the colorimeter cups, and compared. The reference standard was water[27] for those indicators whose acid form is colorless, and 96% sulfuric acid or 70% per-

[19] Witt, *Ber.*, **8**, 820 (1875).

[20] Janowsky, *Monatsh.*, **7**, 124 (1886).

[21] Bamberger and Hübner, *Ber.*, **36**, 3803 (1903).

[22] Beilstein and Kuhlberg, *Ann.*, **158**, 341 (1871); Jackson and Ittner, *Am. Chem. J.*, **19**, 6 (1897).

[23] Von Romburgh, *Rec. trav. chim.*, **2**, 105 (1883).

[24] Montagne, *Rec. trav. chim.*, **26**, 281 (1907); Rousset, *Bull. soc. chim.*, [III] **15**, 71 (1896).

[25] Montagne, *Rec. trav. chim.*, **27**, 357 (1908).

[26] Körner, *Jahresber.*, 350 (1875).

[27] With the two most strongly basic indicators, 1 and 2, the water reference solution was made slightly alkaline to prevent ionization of the indicator.

chloric acid for those having colored ions and colorless molecules. From these comparisons the color intensity, I_w or I_h, was calculated by equation 8.

Precision of Measurements.—A series of experiments showed that the method used in adding the indicator is as precise as the colorimetric measurement. The temperature control was found to be within the same precision with all of the indicators used. Absorption of moisture from the air during the colorimetric measurement was found to be negligible except in the range from 97 to 100% sulfuric acid. In this range the cell shown in Fig. 1 was used. Its optically plane ends are fused on. The length of the enclosed column was determined by measurement with a scale, and was checked by colorimetric comparison of two solutions of a dye of known concentration ratio.

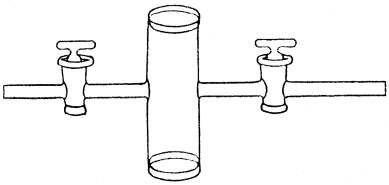


Fig. 1.

The scales of the Klett–Beaver colorimeter,[28] readable to 0.1 mm. were calibrated and found correct to 0.2 mm. In every determination of color intensity the mean of nine independent settings of the instrument was used. The average deviation of the result varies, according to the indicator, from 2 to 5%, at concentrations greater than about 10^{-5} molar. Below this the precision of matching drops off rapidly as the color of a 50-mm. column of liquid becomes very faint.[29] By dilution experiments in a constant medium it was found that within the precision of the color balance: Beer's law applies to the colored form of all the indicators used; the optical system of the colorimeter is accurate; the concentrations of indicator used, never greater than 0.005 molar, do not change the acidity of the sulfuric acid–water mixtures.

The colorimetric purity of the indicators was established in most cases by one or both of the following methods.

A. Constant Specific Color Intensity.—Recrystallization or other purification until the specific color intensity in water or in 96% sulfuric acid was unaffected by a repetition.

B. Congruent Intensity Curves.—The purification process was repeated until repetition produced no change in the intensity composition curves. This test should be very sensitive to an impurity of different base strength or charge type.

Discussion of Results

Table II contains the values of I_w for the series of indicators in sulfuric acid–water mixtures, and Table III those for perchloric acid–water mixtures.[30] The values for the sulfuric acid series are plotted in Figs. 2 and 3.

[28] Beaver, *J. Optical Soc. Am.*, **18**, 41 (1929).

[29] This is in accord with Weber's law of optical sensitivity. Peddie, "Colour Vision," London, 1922, p. 43.

[30] We did not consider it safe to work with solutions of organic compounds in perchloric acid of greater strength than this because of the explosion danger. Even in the range of acidities studied two indicators of our series were found inapplicable to perchloric acid solutions. *p*-Nitrodiphenylamine reacts with the formation of a violet color and a brown flocculent precipitate. Benzalacetophenone appears to be perfectly stable in solutions containing less than 65% acid; above this a fairly rapid decolorization takes place which is not reversed on dilution with water to a composition of 60% acid.

TABLE II

IONIZATION OF INDICATORS IN H_2SO_4–H_2O MIXTURES

% H_2SO_4	I_w	$\log \frac{[BH^+]}{[B]}$	H_0
p-Nitraniline, $s_w = 1.00$			
0.315	0.67	−0.31	+1.73
.473	.59	− .16	+1.56
.939	.43	+ .12	+1.28
2.65	.202	.60	+0.80
3.08	.176	.67	+ .73
3.67	.147	.76	+ .64
4.54	.128	.83	+ .57
5.96	.099	.96	+ .44
8.67	.064	1.17	+ .23
10.59	.046	1.32	+ .08
15.92	.0181	1.73	− .33
23.82	.0057	2.24	− .84
o-Nitraniline, $s_w = 1.00$			
8.69	0.50	0.00	+0.16
19.12	.188	+ .64	− .54
	.181	.71	
23.9	.085	1.03	− .87
31.9	.024	1.50	−1.34
35.4	.016	1.72	−1.57
	.015	1.75	
p-Chloro-*o*-nitraniline, $s_w = 1.00$			
19.12	0.55	−0.08	−0.48
23.90	.34	+ .29	− .85
31.85	.129	.83	−1.39
35.41	.070	1.12	−1.68
41.6	.0247	1.60	−2.16
43.6	.0166	1.77	−2.33
47.8	.0078	2.10	−2.66
48.2	.0077	2.11	−2.67
50.3	.0040	2.40	−2.96
51.5	.0035	2.46	−3.02
p-Nitrodiphenylamine, $s_w = 1.15$			
38.7	0.67	−0.14	−1.95
41.9	.55	+ .04	−2.13
44.2	.42	.24	−2.33
46.3	.311	.37	−2.46
48.8	.193	.70	−2.79
50.8	.116	.95	−3.04
53.7	.057	1.28	−3.37
56.8	.026	1.65	−3.74
58.6	.0116	1.99	−4.08
60.9	.0061	2.27	−4.36

% H_2SO_4	I_w	$\log \frac{[BH^+]}{[B]}$	H_0
2,4-Dichloro-6-nitroaniline, $s_w = 1.00$			
48.2	0.57	−0.12	−2.81
49.4	.47	+ .05	−2.98
50.7	.42	.14	−3.07
53.5	.273	.43	−3.36
56.2	.153	.74	−3.67
60.2	.064	1.17	−4.10
64.3	.0235	1.62	−4.55
p-Nitroazobenzene, $s_h = 0.83$			
	I_h		
41.4	0.096	−0.88	−2.18
43.3	.105	− .84	−2.22
46.6	.156	− .64	−2.42
47.6	.27	− .32	−2.70
	.24	− .39	
50.2	.37	− .10	−2.99
	.39	− .05	
2,6-Dinitro-4-methylaniline, $s_w = 1.00$			
60.1	0.45	+0.09	−3.94
62.0	.38	.21	−4.24
64.1	.22	.55	−4.58
66.3	.170	.69	−4.72
68.6	.077	1.08	−5.11
71.2	.041	1.37	−5.40
73.9	.0183	1.73	−5.76
76.9	.0091	2.04	−6.07
2,4-Dinitroaniline, $s_w = 1.12$			
59.5	0.64	−0.12	−3.97
60.2	.61	− .09	−4.03
	.57	− .02	
62.2	.42	+ .22	−4.31
63.5	.39	.27	−4.36
64.3	.30	.44	−4.53
66.4	.191	.69	−4.78
68.1	.116	.94	−5.03
73.3	.024	1.56	−5.65
N,N-Dimethyl-2,4,6-trinitroaniline, $s_w = 1.21$			
64.1	0.67	−0.09	−4.31
65.1	.53	+ .11	−4.51
66.3	.43	.24	−4.64
67.4	.31	.46	−4.86
68.6	.218	.66	−5.06
69.9	.139	.89	−5.29
71.2	.076	1.17	−5.57
72.6	.047	1.39	−5.79
73.8	.027	1.64	−6.08

TABLE II (*Concluded*)

% H_2SO_4	I_h	$\log \frac{[BH^+]}{[B]}$	H_0
Benzalacetophenone, $s_h = 1.00$			
56.2	0.0187	−1.72	−3.60
57.9	.028	−1.54	−3.78
59.7	.046	−1.32	−4.00
63.7	.128	− .83	−4.49
68.2	.23	− .52	−4.80
73.5	.43	− .12	−5.20
β-Benzoylnaphthalene, $s_h = 1.00$			
	I_h		
59.7	0.028	−1.54	−4.09
63.7	.062	−1.18	−4.45
65.9	.124	− .85	−4.78
68.2	.173	− .68	−4.95
73.2	.48	− .04	−5.59
73.5	.51	+ .02	−5.65
p-Benzoyldiphenyl, $s_h = 1.00$			
67.0	0.078	−1.07	−4.83
67.7	.093	−0.99	−4.91
68.9	.14	− .79	−5.11
70.1	.16	− .72	−5.18
71.4	.29	− .39	−5.51
72.8	.34	− .29	−5.61
74.2	.46	− .07	−5.83
6-Bromo-2,4-dinitroaniline, $s_w = 1.35$			
76.9	0.79	−0.16	−6.07
	.88	− .29	
78.4	.64	+ .04	−6.34
80.1	.48	.26	−6.56
81.8	.28	.58	−6.88
83.6	.159	.87	−7.17
85.4	.110	1.05	−7.35
87.4	.059	1.34	−7.64
89.4	.040	1.51	−7.81
91.5	.025	1.73	−8.03
93.8	.0143	1.97	−8.27
Anthraquinone, $s_h = 1.20$			
77.0	0.0193	−1.79	−6.07
78.4	.029	−1.61	−6.25
80.1	.053	−1.34	−6.52
81.6	.136	− .90	
	.084	−1.12	−6.83
	.097	−1.06	
82.1	.108	−1.01	−6.85
83.6	.206	− .68	−7.10
	.154	− .83	
85.4	.29	− .50	−7.36
87.4	.44	− .24	−7.62
89.4	.57	− .04	−7.82
91.5	.77	+ .25	−8.11
93.8	.91	+ .50	−8.36
2,4,6-Trinitroaniline, $s_w = 1.66$			
96.1	1.21	−0.43	−8.57
98.15	0.80	+ .04	−8.96
98.42	.77	.06	−9.06
98.95	.55	.31	−9.31
99.31	.33	.61	−9.61
99.54	.32	.62	−9.62
99.71	.19	.89	−9.89
99.78	.18	.92	−9.92
99.81	.16	.97	−9.97
99.86	.145	1.02	−10.02
99.88	.085	1.27	−10.27
99.95	.071	1.35	−10.35
99.98	.052	1.50	−10.50
99.99	.053	1.49	−10.49
	.054	1.48	
100.00	.041	1.60	−10.60
100.1	.035	1.67	−10.67

The shape of these curves is obviously due to the super-position of two effects: the steep part of the curve to changing ionization ratio, C_{BH^+}/C_B; the gradual change preceding or following the steep part to the effect of the changing medium on the color intensity of the colored form (S). Comparison of the curves of different indicators shows that the value of S may be expected to change only to a small extent over the range in which the ionization ratio is measurable. We have, therefore, assumed it constant over this range for each indicator, and have set its value equal to the value of I at the point on the curve marked by the circle (Figs. 2 and 3), deter-

mined on a sufficiently large scale plot.[31] The values of S for each indicator and for both solvent series are given in the tables. That the medium

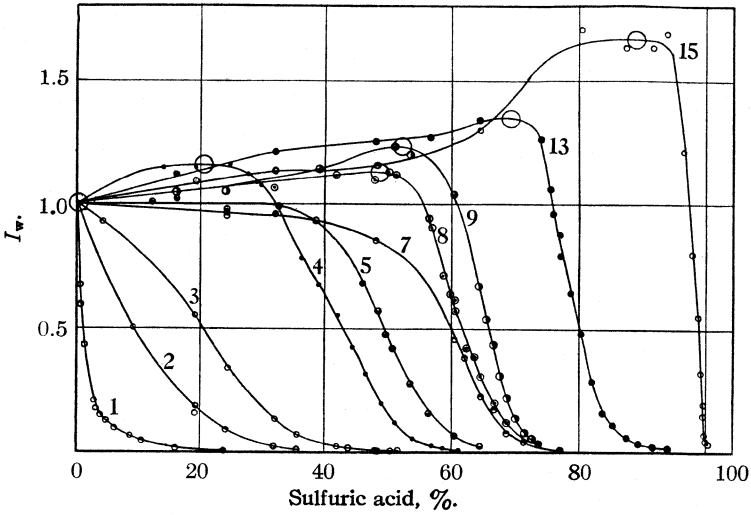


Fig. 2.

effect of the two acids is quite different is shown by the differences of the values of S for a given indicator. From these values the quantities log (C_{BH^+}/C_B) given in the tables are calculated by equation 10 or 11. The results for the sulfuric acid series are plotted against the weight per cent. of acid in Fig. 4.

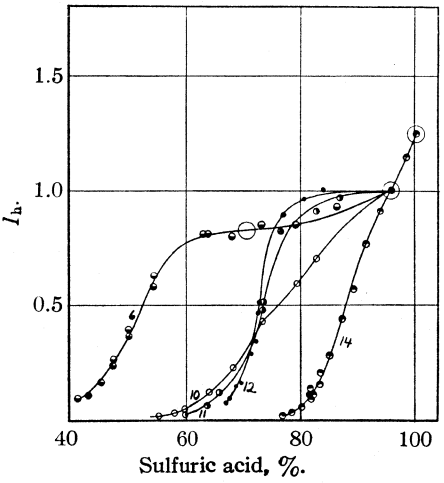


Fig. 3.

By equation 3 these curves should be parallel and the constant difference in ordinates between the curves of two indicators should equal the difference in base strengths in pK' units. The degree of parallelism is very satisfactory except in the range from 65 to 80%. As measured by the curve for picramide (15) in Fig. 1, this is the region in which the medium effect is greatest, and in which therefore the error in the determination of S may be expected to be greatest.

[31] In the case of anthraquinone, S was taken as the relative color intensity in 100% sulfuric acid, although a definite maximum in the intensity curve is not evident, since anthraquinone has been found to be completely ionized in this medium.

It seems reasonable therefore to suppose that this failure of parallelism is due to variation of S rather than to inapplicability of our fundamental assumption embodied in equation 3.

By the step method the relative values of pK' thus obtained were all referred to that of *p*-nitraniline, for which a provisional value of +1.40 was adopted.[32] The values for the sulfuric acid and the perchloric acid series are contained in Table I. There are also included the values obtained by a similar comparison in solutions of sodium formate and of benzene sulfonic acid in anhydrous formic acid, taken from a following paper. We thus have three independent determinations of the pK' values

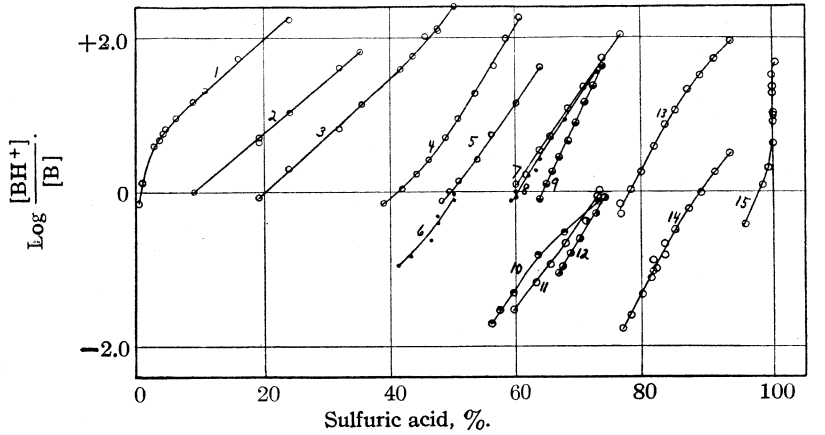


Fig. 4.

of a number of our indicators. The excellent agreement between the three sets of values is the best possible justification of the assumptions made in calculating them, and is sufficient demonstration of the possibility of measuring by means of properly chosen indicators an acidity function which is independent of the indicator used for measuring it, and of using in one solvent system an indicator series calibrated in another.

That the agreement is so much better than might be expected from

[32] This was obtained by averaging the values in the literature for the observed pK' of *p*-nitraniline together with the calculated values obtained by adding the difference in pK' of *o*- and *p*-nitraniline read from Fig. 4 to the observed values for *o*-nitraniline. The error may be ±0.5 unit, since the existing values for these constants have been obtained in fairly concentrated electrolyte solutions and are not very concordant. The observed values are: 2.03, Löwenherz, *Z. physik. Chem.*, **25**, 385 (1898); 1.8, Reinders, THIS JOURNAL, **52**, 5124 (1930); 1.0, Farmer and Warth, *J. Chem. Soc.*, **85**, 1713 (1904); Kuhn and Wassermann, *Helv. chim. acta*, **11**, 3 (1928). Those calculated from the pK' of *o*-nitraniline are: 1.3, Löwenherz, *loc. cit.*; Goldschmidt and Ingebrechtsen, *Z. physik. Chem.*, **48**, 435 (1904); 0.94, Farmer and Warth, *loc. cit.*; Kuhn and Wasserman, *loc. cit.*

previous work[33] may perhaps be due to some extent to the choice of media. Nevertheless, the deforming action upon the molecules of the indicator of the two acid–water mixtures is quite different, as is shown by the differences in the S values for a given indicator. And with formic acid we are dealing with anhydrous solutions of low total ion concentration, even though in a good ionic solvent; with the aqueous mixtures we have extremely large ionic concentrations. There is, however, good reason to expect that the agreement of these colorimetric values should be better than is the case with existing results from electrometric or conductivity data. The relative ionizations of two indicators may be compared in what is practically a single medium, because the concentration of the indicator is too small to affect the medium properties. In the electrometric and conductivity data

TABLE III

IONIZATION OF INDICATORS IN $HClO_4$–H_2O MIXTURES

% $HClO_4$	I_w	$\log \frac{[BH^+]}{[B]}$	H_0
p-Nitraniline, s_w = 1.00			
5.96	0.105	+0.93	+0.47
7.5	.089	1.01	+ .39
9.9	.054	1.24	+ .16
11.9	.034	1.45	− .02
	.038	1.40	
14.9	.024	1.61	− .21
17.0	.019	1.71	− .29
	.021	1.67	
o-Nitraniline, s_w = 1.00			
11.9	0.46	+0.07	+0.03
14.9	.33	.31	− .21
16.8	.284	.40	− .30
19.8	.210	.58	− .48
19.9	.211	.57	− .47
22.1	.168	.69	− .59
23.8	.131	.82	− .66
	.149	.76	
25.9	.119	.87	− .77
29.8	.058	1.21	−1.11
33.1	.0360	1.43	−1.33
35.0	.0264	1.57	−1.47
37.2	.0174	1.75	−1.65
p-Chloro-*o*-nitraniline, s_w = 1.00			
23.8	0.45	+0.09	−0.71
29.8	.249	.48	−1.10
33.1	.170	.69	−1.31
35.0	.124	.85	−1.47
37.2	.086	1.03	−1.65
39.7	.057	1.22	−1.84
42.5	.0277	1.55	−2.17
45.8	.0130	1.88	−2.50
46.3	.0096	2.01	−2.63
46.5	.0096	2.01	−2.63
2,4-Dichloro-6-nitroaniline, s_w = 0.79			
46.9	0.49	−0.21	−2.68
48.4	.41	− .04	−2.85
50.2	.270	+ .29	−3.18
52.1	.169	.56	−3.45
54.1	.091	.89	−3.78
56.2	.049	1.18	−4.07
57.4	.030	1.40	−4.29
58.6	.019	1.61	−4.50
2,4-Dinitroaniline, s_w = 1.00			
56.2	0.57	−0.13	−4.01
58.6	.28	+ .41	−4.55
61.1	.117	.88	−5.02
63.9	.047	1.31	−5.45
p-Nitroazobenzene, s_h = 1.00			
	I_h		
41.7	0.116	−0.88	−2.18
42.5	.136	− .80	−2.26
44.3	.14	− .79	−2.27
47.3	.25	− .48	−2.58
50.6	.44	− .11	−2.95

[33] According to Halford, THIS JOURNAL, **53**, 2944 (1931), the difference between the pK' values for two bases may vary by as much as one unit from solvent to solvent.

the substance whose basicity is being measured changes the nature of the medium to an extent which may be large and specific in solvents of low dielectric constant.[34]

The values of the acidity function, H_0, have been calculated for each indicator for the various sulfuric and perchloric acid mixtures in which it has been used. They are included in Tables II and III, and are plotted in Fig. 5. The numbered horizontal lines in this figure represent the range of

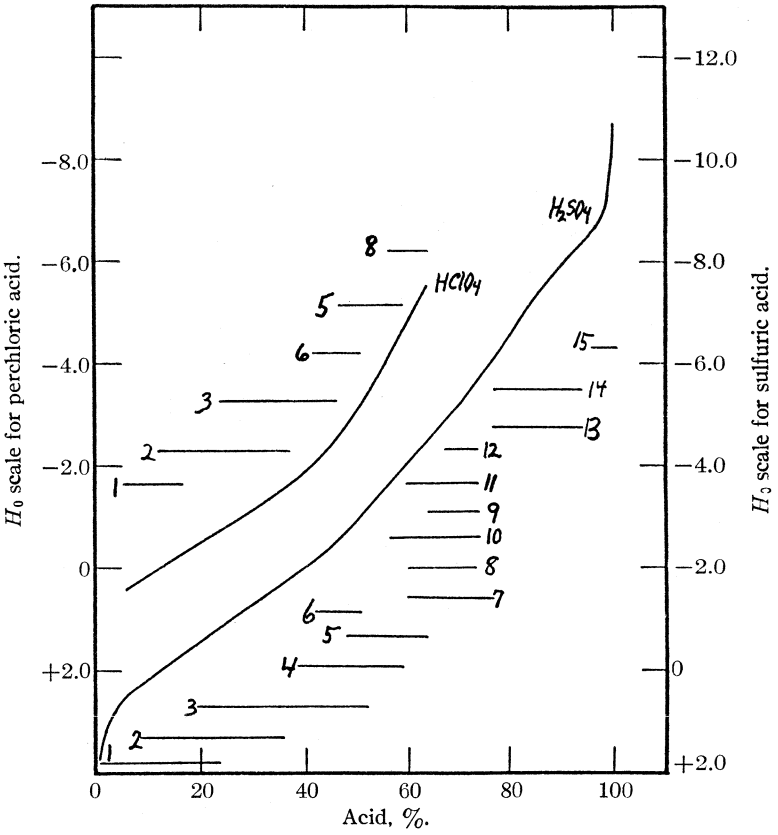


Fig. 5.

solutions in which the corresponding indicator could be employed. The curves for the two acids are nearly coincident, which is somewhat surprising (even though the equivalent weights are nearly the same in this range of acidity) especially because of the difference in the medium effects upon specific color intensity.

Except in the immediate neighborhood of pure water and pure acid, where rapid change is to be expected on a logarithmic plot, the curve is

[34] See Conant and Werner, THIS JOURNAL, **52**, 4436 (1930).

strikingly free from sudden changes of direction. This is true even in the region of the composition $H_2SO_4 \cdot H_2O$, and is another reason for thinking that the lack of parallelism of the curves in Fig. 4 in the region from 65 to 80% acid is due to changing S values instead of to differences in the ratio f_{BH^+}/f_B for different indicators, for large specific effects upon activity coefficients are to be expected only in a region where there is a large change in all activity coefficients. This can, of course, be checked by the use of some other medium in this range of acidity.

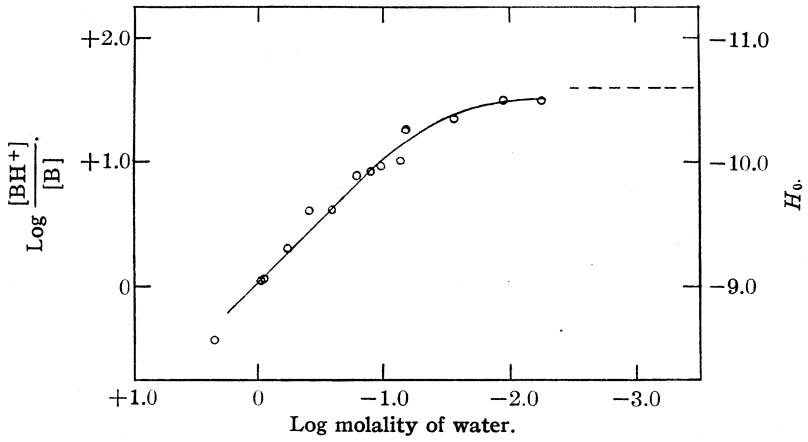


Fig. 6.

The data in the neighborhood of 100% sulfuric acid are plotted in Fig. 6 against the logarithm of the stoichiometric molal concentration of water. From this the acidity of pure sulfuric acid and the concentration of HSO_4^- in the pure solvent may be calculated. It may be shown that

$$\log \frac{C_{BH^+}}{C_B} + \log (x + c_w) = K - \log \frac{f_{BH^+} \cdot f_{HSO_4^-}}{f_B \cdot a_{H_2SO_4}}$$

where x is the concentration of HSO_4^- produced by self-ionization of the solvent, c_w is the stoichiometric concentration of water, and $(x + c_w)$ must equal the total concentration of HSO_4^- since water is a strong electrolyte in sulfuric acid.[35]

At high values of c_w the slope of the curve should be unity, as it is, if the activity coefficients are constant. As c_w approaches zero, log (C_{BH^+}/C_B) should approach asymptotically a limiting value, which is the case. From the limiting value the acidity function, H_0, for pure sulfuric acid is -10.60, 17.6 units more acid than pure water. From the values of the ionization ratio and of c_w in the region where x is negligible, K may be calculated; and from this, again on the assumption of constant activity coefficients, the concentration of HSO_4^- in pure sulfuric acid. The value, 0.027 molal,

[35] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907).

is in agreement with cryoscopic and conductivity evidence of the high self-ionization of sulfuric acid.

Some Kinetic Applications

There are two chief ways in which such a series of indicators as this may be expected to be useful. One is the determination of the strengths of bases and of acids too weak and too strong, respectively, to permit measurement in aqueous solutions; some examples of this are given in the following paper on formic acid solutions. The other is in the interpretation of re-

TABLE IV

A. Condensation of benzoyl benzoic acid, Gleason and Dougherty, THIS JOURNAL, **51**, 310 (1929)

% H_2SO_4	log k 75°	H_0 25°	log k + H_0
90	−2.29	−7.85	−10.14
86	−2.75	−7.32	−10.07
83	−2.89	−6.92	− 9.81
81	−3.23	−6.65	− 9.88
79	−3.53	−6.35	− 9.88
76	−4.06	−5.94	−10.00

B. Beckmann transformation of acetophenone oxime, Lobry de Bruyn and Sluiter, *Kgl. akad. wetenschappen, afdeling der wis- en naturkund*, **13**, 813 (1904)

% H_2SO_4	log k 60°	H_0 25°	log k + H_0
93.6	−2.96	−8.36	−11.32
94.6	−2.89	−8.48	−11.37
97.2	−2.42	−8.84	−11.26
98.7	−2.15	−9.18	−11.33

C. Decomposition of malic acid, Whitford, THIS JOURNAL, **47**, 953 (1925); Dittmar, *ibid.*, **52**, 2746 (1930)

m H_2O	log k 40°	H_0 25°	log k + H_0
0.335	−1.22	−9.50	−10.72
.600	−1.39	−9.25	−10.64
.932	−1.64	−9.07	−10.71
1.59	−1.98	−8.92	−10.90

D. Decomposition of formic acid, Schierz, *ibid.*, **45**, 447 (1923)

% H_2SO_4	log k 25°	H_0 25°	log k + H_0
85	−0.12	−7.20	−7.32
89.2	+ .38	−7.75	−7.37
91.8	+1.02	−8.11	−7.09
94.5	+1.50	−8.47	−6.97
97.6	+2.03	−8.89	−6.86
98.9	+2.51	−9.25	−6.74

E. Decomposition of oxalic acid, Lichty and Bredig, *Z. Elektrochem.*, **12**, 450 (1906). Lichty, *J. Phys. Chem.*, **11**, 225 (1907)

% H_2O	log k 70°	H_0 25°	log k + H_0
0.60	−1.74	−9.51	−11.25
.70	−1.88	−9.42	−11.30
.80	−1.99	−9.38	−11.37
1.00	−2.17	−9.29	−11.46
1.20	−2.31	−9.20	−11.51
1.50	−2.50	−9.12	−11.62
2.00	−2.70	−8.99	−11.69
3.00	−3.03	−8.82	−11.85

F. Decomposition of triphenylacetic acid, Dittmar, *ibid.*, **33**, 533 (1929)

m H_2O	log k 12°	H_0 25°	log k + H_0
1.77	−0.87	−8.75	− 9.62
1.90	− .95	−8.68	− 9.63
2.11	−1.09	−8.66	− 9.75
2.37	−1.22	−8.63	− 9.85
2.93	−1.49	−8.56	−10.05
2.94	−1.50	−8.55	−10.05
3.54	−1.80	−8.40	−10.20
4.18	−2.18	−8.26	−10.44

G. Decomposition of citric acid, Wiig, THIS JOURNAL, **52**, 4729 (1930)

% H_2O	log k 25°	H_0 25°	log k + H_0	% H_2O	log k 25°	H_0 25°	log k + H_0
1.00	−0.61	−9.28	− 9.89	2.97	−1.60	−8.76	−10.36
1.27	− .81	−9.18	− 9.99	3.54	−1.81	−8.63	−10.44
1.84	−1.11	−9.02	−10.13	4.44	−2.14	−8.59	−10.73
2.41	−1.38	−8.88	−10.26	5.23	−2.38	−8.52	−10.90

action velocity data. For a preliminary survey we may use the considerable amount of data on reaction velocities in sulfuric acid–water mixtures, which are summarized in Table IV. In the light of our determination of the acidity of these solutions the reactions may all be considered to be acid catalyzed, since they are reactions whose velocity increases with increase in acidity.[36]

An exact parallelism between the reaction velocity and the acidity can only be expected if the velocity is proportional to the concentration of the ion formed by the addition of one hydrogen ion to one molecule of the neutral substrate, if the ratio of the concentration of this ion to the total concentration of substrate is small, and if there is no further ionization by addition of another hydrogen ion. If these conditions are fulfilled, the equation

$$H_0 + \log k = \text{constant}$$

where k is the velocity constant, should hold.

From the fact that the equation does hold in three of these cases, the decomposition of malic acid, the condensation of *o*-benzoylbenzoic acid and the Beckmann transformation of acetophenone oxime, it may be concluded that the necessary conditions are fulfilled for these reactions. The significance for studies of acid catalysis of measurements of acidity with basic indicators is thus demonstrated.[37]

We wish to acknowledge assistance in this investigation made possible by the generosity of Mr. and Mrs. Reginald Auchincloss.

Summary

It is shown that a significant measure of differences in acidity in one solvent or between solvents may be obtained by means of a properly chosen series of indicators of the same charge type.

The conditions both experimental and in principle for the precise measurement of acidity by indicators are defined.

A series of simple basic indicators is developed by means of which any acidity lying in the range between that of dilute aqueous solutions and that of pure sulfuric acid and in any solvent may be determined.

The acidities of mixtures of sulfuric acid and water from 0 to 100% acid and of perchloric acid and water from 0 to 70% acid are determined and some applications of the results discussed.

[36] This may be considered a more specific statement of Wiig's conclusion (*loc. cit.*) on the basis of Taylor's theory of negative catalysis, *J. Phys. Chem.*, **27**, 322 (1923), that the substrate forms an addition compound with the sulfuric acid, and that water inhibits the reaction by decreasing the concentration of this compound.

[37] We justify this preliminary comparison of reaction velocities determined at one temperature with acidities determined at another by the probability that both relative reaction velocity and relative acidity are little influenced by temperature. Whitford (*loc. cit.*) found the temperature coefficient of the reaction in the malic acid case independent of the composition of the solution.

Because of a parallelism between the acidity and the rates of certain reactions in strong sulfuric acid–water mixtures, these reactions are characterized as acid-catalyzed; the "inhibition" produced by water is ascribed to its basic character.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE KINETICS OF THE THIOCYANATE–BROMINATED FATTY ACID REACTIONS

BY VICTOR K. LA MER AND JOSEPH GREENSPAN

RECEIVED MARCH 11, 1932 PUBLISHED JULY 6, 1932

In their study of the kinetics of the replacement of bromine in brominated propionic ions by thiosulfate ion, La Mer and Kamner[1] found a greater velocity constant when the bromine was in the beta position than when it was in the alpha position, whereas the customary greater reactivity of the alpha position over the beta position was exhibited when the uncharged fatty acid esters were used instead of the sodium salts. This reversal in reactivity was predicted on the basis of the effect of electrostatic repulsions between the ions of the same sign upon the frequency of collisions.[2]

The analogous reactions in which thiocyanate ion[3] is employed as the replacing ion instead of thiosulfate ion appeared to be well adapted for extending the study, particularly since the analytical method for the determination of thiocyanate published recently by Pagel and Ames[4] possesses the advantages of precision and speed over the tedious method employed by Holmberg.

In Table I are given two typical runs for the reaction

$$SCN^- + CH_2BrCOO^- \longrightarrow CH_2(SCN)COO^- + Br^-$$

in the presence of sodium as cation. The k values are the bimolecular constants; the units, liters per mole per minute; $T = 25.00 \pm 0.05°$. The concentration of CNS^- in an aliquot at any time, t, was determined

TABLE I

Run 8 a = 0.1000 m./l. NaCNS, b = 0.1000 m./l. NaBrAc					Run 5 a = 0.04980 m./l. NaCNS, b = 0.04980 m./l. NaBrAc				
t	$a-x$	x	% Conv.	k	t	$a-x$	x	% Conv.	k
122	0.07703	0.02297	23	0.0244	260	0.03917	0.01063	22	0.0210
242	.06344	.03656	37	.0238	517	.03247	.01733	35	.0208
362	.05393	.04607	46	.0236	1333	.02096	.02884	58	.0207
482	.04698	.05302	53	.0234	1575	.01898	.03082	62	.0207
662	.03939	.06061	61	.0232	1940	.01674	.03306	66	.0205

[1] La Mer and Kamner, THIS JOURNAL, **53**, 2832 (1931).

[2] La Mer, *Chem. Reviews*, **10**, 179 (1932); see pp. 207–210.

[3] Holmberg, *Z. physik. Chem.*, **97**, 134–157 (1921).

[4] Pagel and Ames, THIS JOURNAL, **52**, 2698 (1930).

by iodimetric oxidation in borax buffer solution under conditions specified by Pagel and Ames.[4]

An examination of this table shows a downward drift for k amounting to about 4% in the region 23 to 60% conversion. Upon attempting to follow the course of this reaction in more dilute solution to compare the Brönsted–Debye limiting slope with the observed values, the drift became greatly magnified, as illustrated in abbreviated form in Table II.

TABLE II

Run 11 NaBr acetate $a = b = 0.004950$ m./l.			Run 18 NaαBr-propionate $a = b = 0.04950$ m./l.			Run 25 NaβBr-propionate $a = b = 0.009910$ m./l.		
t	% Conv.	k	t	% Conv.	k	t	% Conv.	k
3736	23	0.0153	5298	21	0.000973	7319	18	0.00312
9753	40	.0139	15251	25	.000441	21696	25	.00156

Titration of the solutions initially neutral showed that both the α- and β-bromopropionate–thiocyanate solutions had become acid (approximately P_H 3) whereas the bromoacetate–thiocyanate solutions still remained neutral. This clearly demonstrated the occurrence of side or consecutive reactions. In one run (No. 18 above), SCN^- was found to be regenerated, indicating either an hydrolysis of the resultant thiocyano compound

$$CH_3CH(SCN)COO^- + H_2O \longrightarrow CH_3CH(OH)COO^- + HSCN$$

with consequent increase in acidity of the solution, or an interference of secondary products with the analytical determination of SCN^-.

Ostwald,[5] using conductivity methods, showed that the reaction

$$\underset{\text{(Thiocyanoacetic acid)}}{CH_2(SCN)COOH} + HOH \longrightarrow \underset{\text{(Thiocarbamine-glycolic acid)}}{CH_2(SCONH_2)COOH}$$

was 90% complete in five days (room temperature) at a concentration of 1 mole in 1024 liters. In a recent paper, Fredga[6] demonstrated that the α- and β-thiocyanopropionic acids were also unstable in aqueous solution, undergoing hydration to the corresponding thiocarbamine acids, which might interfere with the analytical method. The increasing acidity of the solution can be explained by the direct hydrolysis of the brominated acids, the monomolecular constants for the α and β cases being of the order of 10^{-5} and 10^{-4}, respectively.[7]

Holmberg's[3] studies involved the reaction $CH_2ICOO^- + SCN^- \xrightarrow{K^+} CH_2SCNCOO^- + I^-$ for concentrations as dilute as 0.0125 M in the iodoacetic salt. The iodo derivative reacts about 50% faster than does the corresponding bromo derivative,[8] so that measurements could be completed within forty-eight hours. Within this period Holmberg obtained no drift in k, whereas we observed a perceptible drift over this same time interval

[5] Ostwald, *Z. physik. Chem.*, **3**, 179–181 (1889).

[6] Fredga, *J. prakt. Chem.*, **231** (N. F.), **123**, 110–128 (1929).

[7] Ref. 1, p. 2844.

[8] See Ref. 2, p. 203.

(Table I). We attribute this difference to the more precise analytical method used by us. In but one measurement extending over fifty hours did Holmberg[9] observe a drift; this he attributes to the formation of the thiocarbamine acid

TABLE III

Na α-bromopropionate a = 0.05215 m./l. NaSCN b = 0.03528 m./l.			Na β-Bromopropionate a = 0.05223 m./l. NaSCN b = 0.03017 m./l.		
t	% Conv.	k	t	% Conv.	k
1297	6	0.000899	1342	20	0.00326

Since interference from end-products will be at a minimum during the first few hours of reaction, we may conclude from Table III that the β-ion reacts about 3.4 times more rapidly than the α-bromopropionate ion, a result in good accord with that obtained for the thiosulfate reaction.[1]

Summary

Side and consecutive reactions obscure the kinetics of the halogen replacement by thiocyanate ion in the halogenated fatty acids when the elapsed time exceeds 1500 minutes. The greater reactivity of halogen in the beta position in an ion has been confirmed for the thiocyanate ion replacement reaction.

[9] Ref. 3, p. 155.

NEW YORK CITY

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE, SODIUM CHLORIDE, LITHIUM CHLORIDE AND HYDROCHLORIC ACID AT 25° BY THE MOVING BOUNDARY METHOD[1]

BY L. G. LONGSWORTH

RECEIVED MARCH 17, 1932 PUBLISHED JULY 6, 1932

Introduction

In the paper following this one, the conductance and transference data for aqueous solutions of some binary electrolytes will be interpreted from the standpoint of the modern theories of solutions. The transference data obtained for that study were determined by the moving boundary method. The experimental work involved in their measurement is the subject of this paper. An equation which is useful for interpolation and extrapolation to zero concentration is also given.

[1] A portion of the work here reported was completed while the author was a National Research Council Fellow.

Apparatus

The moving boundary cell used in making the measurements is shown in Fig. 1. It is similar to the one described in an earlier paper[2] in that either rising or falling boundaries may be formed by the shearing mechanism devised by MacInnes and Brighton.[3] It has two measuring tubes, A and B, of different cross section, in either of which boundaries may be formed. The lower glass plate C is also provided with a cylindrical recess in which a small disk of metal may be inserted, the recess being placed directly beneath a graduated tube. With this addition boundaries of the type described by Cady and Longsworth[4] may be made. Since these boundaries are formed automatically under the action of the electric current, thus requiring no shearing mechanism, they will henceforth be termed "autogenic" boundaries. Tube D carries the electrical connection from the metallic disk.

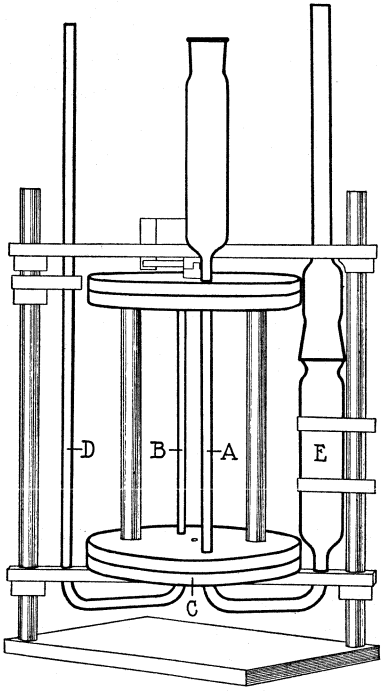


Fig. 1.—The moving boundary cell.

In this new apparatus the electrode chamber E is entirely immersed in the thermostat liquid. This is necessary in order to avoid volume changes due to thermal expansion and contraction which, if allowed to take place, would cause mass displacements of the boundary in the measuring tube.

An important procedure that has not been sufficiently described in previous papers on the moving boundary method as carried out in this Laboratory is the accurate calibration of the graduated tubes. The most recent practice is given below.

The tubes are of Pyrex and are graduated in the manner recommended by MacInnes, Cowperthwaite and Huang.[5] The calibration was made before the tubes were cemented into the supporting framework of the cell. After the graduation marks were etched on a tube a small glass stopcock with a capillary tip was sealed onto it. The tube and stopcock were then very carefully cleaned. Redistilled mercury was drawn from a weighing bottle into the tube until the mercury meniscus roughly coincided with a graduation on the tube. The exact position of the meniscus with respect to the adjacent graduation was determined to the nearest 0.002 millimeter (by a device which will be described immediately) the bottle with remaining mercury weighed, and the meniscus then roughly adjusted to another graduation and the distance from meniscus to graduation again determined. The device for locating the meniscus with respect to a graduation was constructed as follows. A Brown and Sharpe micrometer head which could be read to 0.002 millimeter was adapted to a sliding support which carried the graduated tube, this in turn being clamped to the stage of a microscope with its optical axis in a horizontal position. The tube was thus held in a vertical position

[2] Longsworth, THIS JOURNAL, **52**, 1897 (1930).

[3] MacInnes and Brighton, *ibid.*, **47**, 994 (1925).

[4] Cady and Longsworth, *ibid.*, **51**, 1656 (1929).

[5] MacInnes, Cowperthwaite and Huang, *ibid.*, **49**, 1710 (1927).

and could be moved perpendicularly. A magnification of 40 diameters was employed. With this arrangement it was not necessary to bring the mercury meniscus exactly in line with a graduation, which is an advantage as it is difficult to carry out with tubes of small diameter. In this manner accurate calibrations can be made quite readily. The following figures are the results of five determinations on the volume in milliliters between the first and last graduations of one of the tubes: 1.2114, 1.2112, 1.2108, 1.2110, 1.2108. The mean of these values is 1.2110_4 with a probable error of the mean of 0.00008 ml. The calibration of a tube includes, of course, a determination of the volumes between successive graduations.

Tubes A and B of Fig. 1 have average cross sectional areas of about 0.12 and 0.08 square centimeters, respectively. A third tube, of 0.05 square centimeter area, in a similar cell was also used in some of the measurements.

The constant current regulator and other auxiliary apparatus were the same as described in previous papers.[2] The regulation was accurate to about 0.01%.

Materials.—A good grade of potassium chloride was recrystallized twice from conductivity water, dried and fused. The sodium chloride was precipitated from a saturated solution with pure hydrogen chloride gas, dried and fused *in vacuo*. The best obtainable grade of hydrochloric acid was diluted to constant boiling strength and distilled, the end fractions being rejected. The concentration of this constant boiling acid was interpolated from the data of Foulk and Hollingsworth.[6] The author is indebted to Dr. Shedlovsky for the purification of lithium chloride and preparation of the solutions of this salt. This procedure is described in connection with the conductance measurements on this salt. Solutions were usually prepared by direct weighing of both solute (or concentrated stock solution) and solvent, the concentration being converted to a volume formal basis by means of the density data taken from the "International Critical Tables." Solutions of sodium chloride above 0.02 *N*, however, were prepared in carefully calibrated flasks. All concentrations are expressed in gram equivalents per liter of solution at 25°.

An excellent grade of sodium and potassium salts of tetra-iodofluorescein, which served as indicators in many of the determinations, was furnished by the Eastman Kodak Co. These salts were further purified in this Laboratory by several recrystallizations. The solutions of the indicator electrolytes, the concentrations of which do not need to be known with great accuracy, were prepared in volumetric flasks. The metallic cadmium employed was of "C. P." grade and on qualitative analysis proved to be free from impurities which would yield on solution ions faster than cadmium.

Experimental Procedure

A large proportion of the data was obtained by the Cady and Longsworth method using a cadmium disk anode as mentioned above. Where applicable this is the simplest procedure and gives results of high precision. However, the $CdCl_2$–HCl and $CdCl_2$–KCl boundaries become invisible below 0.01 *N* and the $CdCl_2$–NaCl boundary cannot be detected much below 0.02 *N*. $CdCl_2$–LiCl boundaries were obtained only at 0.05 *N* and above, and even at 0.05 *N* they were diffuse and difficult to locate accurately except at relatively high current densities. Lithium iodate proved to be the most satisfactory indicator for the lithium chloride solutions. To study solutions of sodium chloride and potassium chloride at concentrations lower than those mentioned, the corresponding salts

[6] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

of tetra-iodofluorescein served as indicators, though in special cases other indicators were also used. MacInnes and Brighton's[3] shearing mechanism was used for forming these boundaries. With the tetra-iodofluorescein as indicator boundaries were sharp and readily visible at concentrations considerably below 0.001 *N*. However, as will be shown later, the data obtained on the most dilute solutions are of lower precision due to a large and somewhat ambiguous solvent correction, which was, however, kept at a minimum.

The upper limit of concentration of solutions for which accurate transference numbers have been obtained is 0.2 *N*. At this and to an increasing extent at higher concentrations, the heat developed in the moving boundary cell gives rise to convection currents which tend to distort the boundary and cause mixing. In order to obtain accurate transference numbers at 0.2 *N* it was found necessary to employ the tube of smallest cross sectional area since the actual amount of heat developed is smaller and the area of tube surface exposed to the thermostat is relatively greater. In addition, at 0.2 *N* the volume correction for the processes behind the boundary is in many cases quite large. This correction, as will be shown below, is not an exact one, but has relatively little effect on the results, except in extreme cases.

In order to keep the volume correction as definite as possible one electrode is kept closed. In the case of the autogenic boundaries the anode side is necessarily the closed one. Using sheared boundaries the electrode chamber completely immersed in the thermostat is always the closed side of the system.

Among the advantages of the moving boundary method over the Hittorf method are the rapidity with which measurements can be made and the fact that the progress of the determination can be followed from the beginning. In contrast, a Hittorf determination in which, at best, two figures are obtained, requires several days and the success of a determination is in doubt until the final analyses are completed.

To show the number and relative accuracy of the data obtained in a single determination by the moving boundary method, the figures recorded in a quite typical experiment, lasting about ninety minutes, are given in Table I. It will be recalled that by this method the transference number T is obtained from the formula

$$T = \frac{VCF}{1000\,It}$$

in which V is the volume in milliliters swept through by the boundary in t seconds when a current of I amperes is flowing. C is the concentration and F the faraday in coulombs.

Column 2 of the table gives the time required for the boundary to move through the volume between the etch marks spaced by the distance

in centimeters given in Column 1. Column 3 contains the factor $VCF/1000\ I$, which gives, on division by the value of t in the preceding column, a value of T_+ (Column 4) corresponding to the total volume through which the boundary has moved in that time. The values in Column 4 thus constitute a running check on the progress of the experiment.

TABLE I

THE DATA AND COMPUTATIONS FOR A TYPICAL DETERMINATION

T_+ at 25° for NaCl at $C = 0.02$. Autogenic boundary—Cd anode; Ag·AgCl cathode; current, 0.0016001 ampere.

1 x	2 t	3 $VCF/1000\ I$	4 T_+	5 Δx	6 Δt	7 $VCF/1000\ I$	8 T_+
0.0	0			0.0–10.0	3453	1344.7	0.3894
0.5	172			0.5–10.0	3281	1277.6	.3894
1.0	344	133.9	0.3892	1.0–10.0	3109	1210.8	.3894
1.5	516			1.5–10.0	2937	1142.9	.3891
2.0	689	268.3	.3894	2.0–10.0	2764	1076.4	.3894
3.0	1036	402.8	.3888	0.0– 9.5	3276	1276.4	.3896
4.0	1380	536.5	.3888	0.5– 9.5	3104	1209.2	.3896
5.0		670.6		1.0– 9.5	2932	1142.5	.3897
6.0	2070	805.5	.3891	1.5– 9.5	2760	1074.6	.3894
7.0	2414	939.4	.3891	0.0– 9.0	3104	1208.6	.3894
8.0	2757	1074.6	.3898	0.5– 9.0	2932	1141.5	.3893
8.5	2933			1.0– 9.0	2760	1074.7	.3894
9.0	3104	1208.6	.3894	0.0– 8.5	2933	1142.0	.3894
9.5	3276			0.5– 8.5	2761	1075.0	.3894
10.0	3453	1344.7	.3894	0.0– 8.0	2757	1074.6	.3898
						Mean	0.3894

In Column 5 there are fifteen combinations of readings in which the boundary has traveled eight or more centimeters, and in Column 6 the corresponding times in seconds. Hence, by calculating a value of T_+ (Column 8) for each of these combinations from the data of Columns 6 and 7, errors in individual observations are minimized. The probable error of the mean of this typical experiment is 0.00003, corresponding to an error of 0.3 second. This is, of course, merely an indication of the accuracy of the time observation. Errors may also arise from determinations of the volumes, the current and the concentration. The accuracy of all these measurements is within 0.02%. Uncertainties in the necessary corrections to be described below may also introduce small errors.

Experimental Results and Computations

The results of individual determinations on solutions of the four electrolytes each at a series of concentrations are given in Tables II to V. In general, more than one potential gradient was employed at each concentration, but over a considerable range of voltage no variation in the observed transference number resulted. As will be shown in the following sections these data are subject to corrections, (a) for volume changes

behind the boundary, and (b) for the conductance of the solvent. The magnitudes of these corrections are also given in the tables. Where results are given in the tables for both anion and cation boundaries at the

TABLE II

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE AT 25°

Concn. T_- or T_+	0.001 T_-	0.002 T_-	0.005 T_-	0.01 T_-	0.02 T_-	0.01 T_+	0.02 T_+	0.05 T_+	0.1 T_+	0.2 T_+
Separate determinations	0.5052	0.5074	0.5089	0.5091	0.5095	0.4894	0.4894	0.4894		0.4876
	.5052	.5074	.5083	.5092	.5094	.4893	.4892	.4893		.4876
						.4894	.4890	.4895		.4877
						.4890	.4895	.4896		.4877
							.4894	.4895		
Mean	.5052	.5074	.5086	.5092	.5095	.4893	.4893	.4895		.4877
Vol. corr.	...	...	...	...	...	+.0001	+.0002	+.0004		+.0015
$K_{H_2O} \times 10^{-6}$	1.3	1.3	1.3	1.3	1.3	2.0	2.0	2.0		.....
Sol. corr.	0.0004_5	0.0002_3	0.0009	0.0005	0.0003_3	0.0007	0.0004_4	0.0001_1		.....
T corr.	$.5097$	$.5097$	$.5095$	$.5097$	$.5098$	$.4901$	$.4899$	$.4900$	0.4898[a]	$.4892$
T_+ final	$.4903$	$.4903$	$.4905$	$.4902$	$.4901$	.....	.....	$.4900$	$.4898$	$.4892$

[a] This value is based on work as reported in a previous paper.[1]

TABLE III

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF SODIUM CHLORIDE AT 25°

Concn. T_- or T_+	0.01 T_-	0.02 T_+	0.05 T_+	0.1 T_+	0.2 T_+
Separate determinations	0.6073	0.3894	0.3872	0.3851	0.3812
	.6073	.3896	.3874	.3850	.3812
	.6078	.3894	.3875	.3851	.3813
	.6072	.3895	.3877	.3850	.3813
	...	.3900	.3875	.3851	...
	...	.3894	.3875	.3850	...
Mean	.6074	.3896	.3875	.3851	.3813
Vol. corr.	+.0001	.0000	+.0001	+.0001	$+.000_1$
$K_{H_2O} \times 10^{-6}$	1.3	2.2	2.2	2.2	...
Sol. corr.	0.0006	0.0004	0.0002	0.0001	...
T corr.	.6081	.3900	.3878	.3853	$.3814$
T_+ final	.3919	.3900	.3878	.3853	$.3814$

TABLE IV

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF LITHIUM CHLORIDE AT 25°

Concn. T_- or T_+	0.0098356 T_-	0.011104 T_-	0.018515 T_-	0.032550 T_-	0.049942 T_-	0.064021 T_-	0.10000 T_-	0.064021 T_+	0.10000 T_+
Separate determinations	0.6699	0.6703	0.6732	0.6764	0.6784	0.6797	0.6829	0.3200	0.3166
	.6695	.6701	.6726	.6759	.6783				.3169
	.6700		.6729	.6757					.3172
			.6731	.6760					.3170
Mean	.6698	.6702	.6729	.6760	.6783	.6797	.6829	.3200	.3169
Vol. corr.	.0001	.0001	.0002	.0003	.0005	.0006	.0010	.0000	−.0001
$K_{H_2O} \times 10^{-6}$	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sol. corr.	0.0010	0.0010	0.0005	0.0003	0.0002	0.0002	0.0001	0.0001	....
T corr.	.6709	.6713	.6736	.6766	.6790	.6805	.6840	.3201	0.3168
T_+ final	.3291	.3287	.3264	.3234	.3210	.3198	.3167	...	...

TABLE V

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID AT 25°

Concn.	0.01 T_+	0.02 T_+	0.05 T_+	0.1 T_+
Separate determinations	0.8247	0.8260	0.8287	0.8303
	.8249	.8260	.8285	.8302
	.8247	.8258	.8289	.8308
		.8261	.8285	.8301
				.8305
Mean	.8248	.8260	.8287	.8305
Vol. corr.	+.0001	+.0002	+.0005	+.0009
$K_{H_2O} \times 10^{-6}$	1.3	1.3	...	...
Sol. corr.	0.0003	0.0002	...	...
T_+ final	$.825_2$	$.826_4$	$.829_2$	$.831_4$

same concentration, a mean value of T_+ has been taken, and is recorded under the heading T_+ final.

(a) **The Volume Correction.**—G. N. Lewis[7] has shown that the observed transference number must be corrected for a displacement of the boundary due to volume changes behind the boundary. This correction is most readily applied by means of the equation

$$T = T_{obs.} + \frac{C\Delta V}{1000}$$

where ΔV is this volume change in milliliters per faraday equivalent and C is the concentration. For the cation boundaries the volume change, ΔV_+, is

$$\Delta V_+ = \frac{1}{2}\overline{V}_{CdCl_2} - T_+\overline{V}_{XCl} - \frac{1}{2}V_{Cd}$$

in which the $\overline{V}$'s are partial molal volumes and V is an atomic volume. The subscripts indicate the salt involved and X may stand for H, K, Na or Li. For the anion boundaries a silver–silver chloride cathode was employed and the volume change, ΔV_-, is

$$\Delta V_- = V_{Ag} + T_+\overline{V}_{XCl} - V_{AgCl}$$

In a recent paper E. R. Smith[8] has found experimentally the value of ΔV_- in this reaction, using a potassium chloride solution, and has obtained adequate agreement with the computation as given. This important paper also includes a detailed treatment of the theory of the volume changes affecting the boundary velocity.

The partial molal volumes, which were computed from data in the "International Critical Tables" according to the directions of Lewis and Randall[9] are expressed by the following formulas.

[7] Lewis, THIS JOURNAL, **32**, 862 (1910).

[8] Smith, *Bur. Standards J. Research*, **8**, 457 (1932).

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, p. 36.

$$\overline{V}_{LiCl} = 17.06 + 2.13\sqrt{m}$$
$$\overline{V}_{KCl} = 26.65 + 3.21\sqrt{m}$$
$$\overline{V}_{NaCl} = 22.85 - 5.32\,(0.8105)^m(1 - 0.2101\,m)$$
$$\overline{V}_{HCl} = 18.07 + 1.27\sqrt{m}$$
$$\overline{V}_{CdCl_2} = 23.24 + 8.82\sqrt{m}$$

These empirical expressions are based on the linear variation of the apparent molecular volume, ϕ, with the square root of the molality, m, except that in the case of sodium chloride the function given for that salt represents the data somewhat better than the simple square root relation, and is derived from the equation

$$\phi = 22.85 - 5.32\,(0.8105)^m$$

The three constants of this equation were determined graphically by a method given by Running.[10] It is interesting to note that this function, unlike the square root relation, may be used to compute the partial molal volume of the solute in the hypothetical solution in which no water is present ($m = \infty$),[11] as well as in the infinitely dilute solution ($m = 0$).

The functions given here were developed before the author had noted the appearance of the recent papers by Masson and others,[12] who show the wide validity of the linear variation of ϕ with the square root of the volume formal concentration. Otherwise their formulas could have been directly adapted to the computation of the necessary volume corrections.

In using these equations[13] in computing the corrections recorded in

[10] Running, "Empirical Formulas," John Wiley and Sons, Inc., New York, 1917, p. 28.

[11] A. F. Scott, *J. Phys. Chem.*, **35**, 1410 (1931).

[12] Masson, *Phil. Mag.*, **8**, 218 (1929); Redlich, *Naturwissenschaften*, **19**, 251 (1931); Geffcken, *ibid.*, **19**, 321 (1931); *Z. physik. Chem.*, [A] **155**, 1 (1931); Redlich and Rosenfeld, *ibid.*, [A] **155**, 65 (1931).

[13] Since the partial molal volumes are functions of the concentration and as the concentration distribution in the neighborhood of the electrode is far from uniform, it is evident that the correction as computed above is an approximation. However, the entire correction is small at moderate concentrations so that the error involved in this case cannot be large. In the case of the autogenic boundaries the diffusion layer is well defined and the concentration distribution resulting from pure diffusion and ionic migration is not destroyed by gravity currents as may be the case with the electrode arrangement used with sheared boundaries. Hence in the case of the autogenic boundaries it is theoretically possible to obtain a better estimate of this correction in the following manner. A passage of one faraday of electricity will cause the boundary to move from $X = 0$ (the face of the electrode, of say metallic cadmium) to a point in the tube X_1. The region from $X = 0$ to $X = X_1$ will contain one equivalent of cadmium chloride whose concentration distribution may be computed from formulas developed by Sand [*Phil. Mag.*, **6**, 1, 45 (1901)] and by Miller and Rosebrugh [*J. Phys. Chem.*, **14**, 816 (1912)]. Thus, since C_{CdCl_2} is known as a function of X, and $\overline{V}_{CdCl_2}$ as a function of C_{CdCl_2}, $\overline{V}_{CdCl_2}$ may be expressed as a function of the distance. The definite integral

$$\frac{1}{X_1}\int_0^{X_1} \overline{V}_{CdCl_2}\,dX$$

will then give the average value of the partial molal volume of the cadmium chloride and

Tables II to V the approximation was made that over the range studied, the concentration could be replaced by the molality, m. For the atomic and molecular volumes the following values were used

$$V_{Ag} = 10.3 \qquad V_{Cd} = 13.0 \qquad V_{AgCl} = 25.8$$

(b) **The Solvent Correction.**—Although the necessity for the correction for the conductance of the solvent has been generally recognized in the case of conductivity measurements, apparently no previous investigator has considered the application of such a correction to transference data. Other workers have either considered the data of insufficient accuracy to warrant the application of the correction or have thought that it would be negligible even at the lowest concentrations which they studied. However, with the precision attained by the moving boundary method, such a correction is imperative. Moreover, a solvent correction should be applied to the results of transference measurements made by all of the available methods. Fortunately it has but little effect on the final results except in the most dilute solutions. In that region, however, it may be the factor determining the accuracy of the data.

The necessity for a solvent correction was impressed on the author as a result of the following observations. If anion and cation boundaries are observed independently for the same solution, the value of $(1 - T_-)$ obtained from an anion boundary, T_- being the anion transference number, should exactly equal the cation transference number, T_+. At concentrations above 0.02 N such was found to be accurately the case. As the concentration was decreased, however, the two independently observed values were found to diverge. This is illustrated in Fig. 2, where the observed transference data on the lower concentrations of potassium chloride have been plotted, for convenience, against the cube root of the concentration. Curve A gives values of $(1 - T_-)$ in which T_- is here the observed anion transference number which has been corrected for the volume changes behind the boundary, but not for solvent conductance. Curve B gives corresponding values of the directly determined cation transference number, T_+, to as low a concentration as the boundaries were visible. Curves A and B should coincide and would do so except that at these low concentrations the conducting impurities in the solvent are carrying an appreciable fraction of the total current. Curve C in the figure is a plot of the values of $(1 - T_-)$ and T_+ after being corrected for the solvent conductance according to considerations discussed below.

An expression by which the observed transference number can be corrected for the solvent conductance may be derived as follows. The

this is the value which should be used in computing the volume correction. The computation of the volume correction in this manner, however, is very laborious. The volume corrections actually used are based on a value of C_{CdCl_2} the same as C_{XCl}, that is, an approximate mean, in all probability sufficiently accurate for the purpose.

current I flowing in a linear conductor is equal to the total flux of electricity through a given cross section per unit time. For a solution of a uni-univalent electrolyte at concentration C, V_+ will represent the actual work-

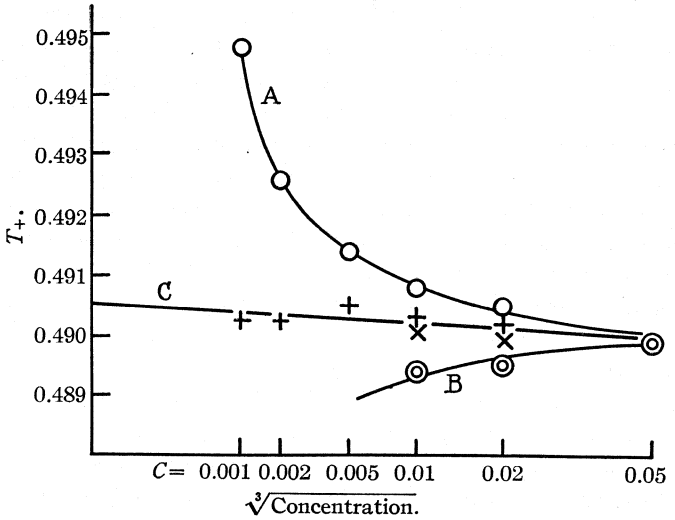


Fig. 2.—Effect of solvent correction on observed transference numbers for potassium chloride solutions: ○, $1-T_-$ (observed); +, $1-T_-$ (corrected); ◎, T_+ (observed); ×, T_+ (corrected).

ing velocity of the entire cation constituent and V_- that of the anion constituent. The total current flowing in a tube of uniform cross section A is

$$I = \frac{CFA}{1000}(V_+ + V_-) + \frac{FA}{1000}\Sigma C_i V_i$$

The last term provides for the current carried by impurities in the solvent, whose unknown concentrations and velocities are C_i and V_i, respectively. On multiplying this equation through by $V_+/(V_+ + V_-)$ and rearranging

$$\frac{V_+}{V_+ + V_-} = T_+ = \frac{CFAV_+}{1000I} + \frac{FA}{1000I} \cdot T_+ \Sigma C_i V_i$$

is obtained. Since the mobility, U_i, of an ion constituent is the ratio of the velocity, V_i, to the field strength, E, this equation may be written

$$T_+ = \frac{CFAV_+}{1000I} + \frac{FEA}{1000I} T_+ \Sigma C_i U_i$$

However, the ratio I/EA is the specific conductance of the solution, K_{solution}, and $(F/1000)\ \Sigma C_i U_i$ is the specific conductance of the solvent, K_{solvent}, which may be measured independently. If the assumption be made that introduction of the solute into the solution does not alter the concentration and mobilities of the impurities in the solvent, this equation becomes

$$T_+ = T_+ \text{(obs.)} + T_+ \frac{K_{\text{solvent}}}{K_{\text{solution}}}$$

for the cation transference number and there is a corresponding expression for the anion transference number.

A determination of the solvent correction in the manner outlined above leads to a value for that correction which is necessarily too small, since the potential gradient in the indicator region is greater than that in the region ahead of the boundary, with the result that this region will be progressively contaminated with impurities forced across the boundary. It was thought that with the data on potassium chloride which were available a better estimate of this correction could be obtained by assigning to the solvent a conductance which, when the corresponding correction was applied to the data, would bring the two curves of Fig. 2 very nearly into coincidence. The solvent conductance as determined in this manner was but slightly higher than the value experimentally measured, and the data, when thus corrected, give Curve C of Fig. 2.

In order to reduce the solvent correction to as low a value as possible the following procedure was devised. The solutions of sodium chloride and potassium chloride below 0.02 normal, on which anion boundaries were observed, were swept out with carbon dioxide-free nitrogen[14] before introduction into the moving boundary cell. This procedure materially improved the quality of the solvent but by no means eliminated the correction since after introduction into the cell a small portion of the solution must necessarily come in contact with the air of the laboratory. Moreover, the solvent contains minute amounts of ionic impurities other than carbonic acid and may also acquire additional impurities from contact with the lubricant used in the assemblage of the cell.[15] The solvent conductance was therefore determined by direct current measurement in the moving boundary cell after the water had been subjected to the same treatment as the solutions being observed. The values for all solvent conductances are recorded in Tables II to V.

Disturbing and Restoring Effects at the Boundary.—A characteristic of the moving boundary method which largely determines the upper limit of concentration at which accurate measurements can be made is the presence of heat and diffusion effects at the boundary. There is, however, a mechanism operating to oppose such disturbances. This is a restoring effect due to the change of the potential gradient at the boundary. This effect has been studied and described by MacInnes and Cowperthwaite.[16] A large difference in the densities of the two solutions meeting at the boundary appears to reinforce this restoring effect. Ob-

[14] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[15] A lubricant which was found to be quite satisfactory was prepared by melting together five parts of vaseline and one part of beeswax. Both ingredients were extracted several times with hot conductivity water before they were mixed.

[16] MacInnes and Cowperthwaite, *Proc. Natl. Acad. Sci.*, **15**, 18 (1929).

viously, to obtain correct transference numbers the restoring effect must be stronger than all the disturbing influences. The indications that this latter condition is fulfilled are (a) the boundaries appear flat and sharp, (b) at constant current they move with constant velocity, (c) the observed transference numbers are, within wide limits, independent of the current density, and (d) independent observations on cation and anion boundaries for the same solution give consistent results. With the exception of condition (d) for hydrochloric acid solutions, as will be explained below, the experiments reported in this paper fulfilled all of these requirements.

Measurements on Solutions of Hydrochloric Acid.—Due to the high mobility of the hydrogen ion the heat effects were more difficult to eliminate in the measurements on hydrochloric acid than in corresponding determinations with solutions of the other electrolytes. In addition any uncertainty as to the values for these salts was eliminated by check measurements on cation and anion boundaries. Such checks were difficult to obtain with hydrochloric acid solutions, since at the high current densities necessary to bring out sharp HIO_3/HCl boundaries, for example, the heat effects are apparently large enough to produce appreciable mixing. It was therefore considered desirable to make confirmatory determinations of the cation transference numbers using indicators other than cadmium chloride. A comparison of the results with the different indicators is made in Table VI. Results, using cadmium chloride as indicator, with three sizes of tube, are also included.

TABLE VI

A COMPARISON OF RESULTS ON HYDROCHLORIC ACID

Concn.	Tube area	Indicator	Cation trans. no., T_+	Concn.	Tube area	Indicator	Cation trans. no., T_+
0.1	0.12	$CdCl_2$[a]	0.8305	0.02	0.08	$CdCl_2$[a]	0.8264
.1	.08	$CdCl_2$[a]	.8311	.02	.08	0.0133 *N* CsCl	.8258
.1	.05	$CdCl_2$[a]	.8314	.02	.08	.0133 *N* TlCl	.8262
.1	.08	0.066 *N* CsCl	.8309	0.01	0.08	$CdCl_2$[a]	0.8252
0.05	0.08	$CdCl_2$[a]	.8292	.01	.08	0.0066 *N* TlCl	.8248
.05	.05	$CdCl_2$[a]	.8291				

[a] Autogenic boundaries.

From the data in this table it is seen that there is a slight increase in the apparent transference number at 0.1 *N* as the tube size is diminished from 0.12 to 0.08 and but little change on further decrease of tube size. Furthermore, the data of Table VI indicate such a slight dependence on the nature of the indicator ion as to be within the limits of error in the determinations. The data obtained in the smallest tube, with cadmium chloride as indicator, though possibly not quite as accurate as the corresponding data for potassium, sodium and lithium chlorides, are probably correct within 0.05%.[17]

[17] The value of T_+ for 0.1 *N* HCl reported in this paper is 0.1% higher than the

Discussion of Results

A comparison between some of the data for potassium chloride given in Table II and that recently obtained by MacInnes and Dole,[18] using the Hittorf method, has already been made by those authors, and showed excellent agreement of the results obtained by the two methods. The earlier work on potassium chloride by Smith and MacInnes[19] and MacInnes and Brighton[3] gave results slightly higher at 0.1 N than those given in this paper, but agreeing within the limit of error at 0.2 N. These researches were, however, carried out before the constant current apparatus was used. After that device was installed, Dr. Cowperthwaite obtained anion and cation results (not published) at 0.1 N with falling boundaries agreeing perfectly with those reported here.

In the case of lithium chloride, the recent careful measurements of Jones and Bradshaw[20] using the Hittorf method are given in Table VII together with values obtained by the moving boundary method on the same salt.

TABLE VII

VALUES OF T_+ FOR LiCl AT 25° AS DETERMINED BY THE HITTORF AND MOVING BOUNDARY METHOD

Concn.	0.01	0.02	0.05	0.1
T_+, L.	.329	.326	.321	.317
T_+, J. and B.	.329	.327	.323	.319

This table shows that there is substantial agreement between the new Hittorf results and the results obtained by the moving boundary method. These new experiments, in addition to those on potassium chloride, furnish ample evidence that the two methods measure the same property of a solution of an electrolyte.[21]

value reported in connection with some work on mixtures of HCl and KCl.[1] This revision affects the magnitude of certain ion conductances reported in the earlier paper but would not alter any of the conclusions.

[18] MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931).

[19] Smith and MacInnes, *ibid.*, **47**, 1009 (1925).

[20] Jones and Bradshaw, *ibid.*, **54**, 138 (1932).

[21] Transference numbers for lithium chloride have also been obtained by the e.m.f. method by MacInnes and Beattie [THIS JOURNAL, **42**, 1117 (1920)] and their data have been recomputed by Jones and Bradshaw. The results for several concentrations may be compared as follows:

Concn.	0.01	0.02	0.05	0.1
T_+, MacInnes and Beattie	.334	.327	.318	.311
T_+, Jones and Bradshaw	.333	.331	.326	.320

A difficulty with the e. m. f. method is that, since the transference numbers change with the concentration, the experimental data must be fitted to empirical or semi-empirical equations. The difference between the transference numbers obtained from the same data using different equations is shown in the figures just given and indicates that the computed transference numbers are very sensitive to the form of the equation chosen. As can be seen the values in Table VII are roughly the mean of the results by the two

Transference Numbers as a Function of the Concentration.—For purposes of interpolation and for extrapolation to zero concentration it is desirable to express the measured transference numbers as a function of the concentration. Dole[22] has recently shown how the Onsager[23] equations for ion conductances may be combined to give an expression for the transference number as a function of the concentration. This expression must be valid in the limiting region of zero concentration if the ion conductance equations are valid and the recent precise conductance measurements of Shedlovsky[24] indicate the accuracy of these limiting laws. Hence a plot of any function which may be derived for transference data must go into the axis of zero concentration with the slope required by the Onsager equations.

For the ions of uni-univalent electrolytes at 25° in water

$$\lambda = \lambda^0 - (\alpha\lambda^0 + \beta)\sqrt{C}$$

In this expression λ is the equivalent conductance of the ion at concentration C, λ^0 the equivalent conductance at zero concentration, and α and β are numerically equal to 0.2274 and 29.90, respectively. The cation transference number, on the basis of this expression, is

$$T_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+^0 - (\alpha\lambda_+^0 + \beta)\sqrt{C}}{\lambda_+^0 + \lambda_-^0 - [\alpha(\lambda_+^0 + \lambda_-^0) + 2\beta]\sqrt{C}} \qquad (1)$$

Since $T_+^0 = \lambda_+^0/(\lambda_+^0 + \lambda_-^0)$ and setting, for abbreviation

$$\Lambda' = \lambda_+^0 + \lambda_-^0 - [\alpha(\lambda_+^0 + \lambda_-^0) + 2\beta]\sqrt{C}$$
$$= \Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{C}$$

Equation (1) may be rearranged to give

$$T_+ = T_+^0 - \frac{(1 - 2T_+^0)}{\Lambda'}\beta\sqrt{C} \qquad (2)$$

This limiting expression for the transference number states that a plot of T_+ against $\sqrt{C}$ should go into the axis of zero concentration with the slope

$$\left(\frac{\mathrm{d}\,T_+}{\mathrm{d}\sqrt{C}}\right)_{C=0} = \frac{2T_+^0 - 1}{\Lambda_0}\beta$$

The limiting slope is thus seen to be proportional to the deviation of T_+^0 from 0.5 and inversely proportional to the limiting conductance, Λ_0, of the electrolyte.

Equation (2) is not valid in the concentration range where the measurements have been made. However, the striking success of the Shedlovsky

methods of calculation. MacInnes and Beattie did not use graphical methods in their computation as Jones and Bradshaw imply. Both methods of calculation are analytical, the difference being in the form of function used.

[22] Dole, *J. Phys. Chem.*, **35**, 3647 (1931).

[23] Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

[24] Shedlovsky, THIS JOURNAL, **54**, 1405, 1411 (1932).

method of treating conductance data suggested the possibility of a similar treatment of transference data. Solution of Equation (2) for T_+^0 gives

$$T_+^0 = \frac{T_+ \Lambda' + \beta \sqrt{C}}{\Lambda' + 2\beta \sqrt{C}}$$

Values of T_+^0 were computed from each pair of observed values for T_+ and C. These computed values of T_+^0—plotted as $T_+^{0\prime}$—were found to vary

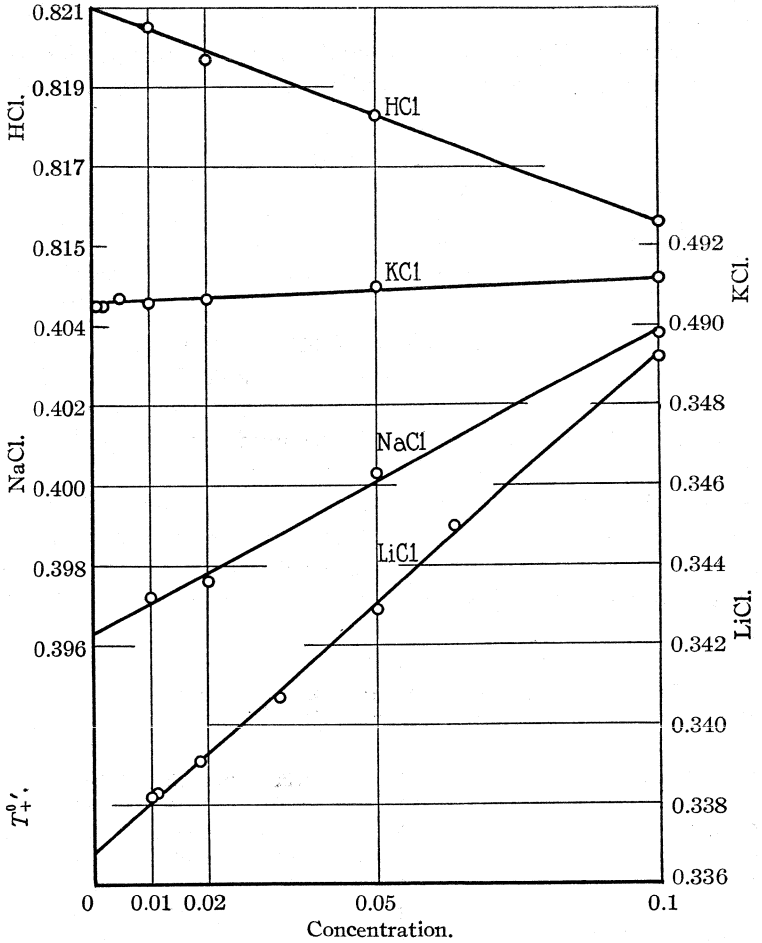


Fig. 3.—Test of Equation (4) and the evaluation of the contants T_+^0 and A.

linearly with the concentration as shown in Fig. 3 up to a concentration of 0.1 normal. Thus $T_+^{0\prime}$ is a linear function of the concentration

$$T_+^{0\prime} = T_+^0 + AC = \frac{T_+ \Lambda' + \beta \sqrt{C}}{\Lambda' + 2\beta \sqrt{C}} \qquad (3)$$

Solution of (3) for T_+ gives

$$T_+ = T_+^0 - \frac{1 - 2T_+^0}{\Lambda'} \beta \sqrt{C} + AC\left(1 + \frac{2\beta\sqrt{C}}{\Lambda'}\right) \qquad (4)$$

an expression for T_+ which has the theoretical limiting slope. A simple interpolation formula which appears to be valid to much higher concentrations than Equation (4) has been proposed and tested by Jones and Dole.[25] Their formula, however, does not in general extrapolate to infinite dilution with the correct limiting slope.

The constants of Equation (4) as obtained from a plot similar to Fig. 3 are given in Table VIII together with the values of Λ_0 given by Shedlovksy.

TABLE VIII

CONSTANTS OF EQUATION (4)

	T_+^0	A	Λ_0
LiCl	0.3368	0.125	115.00
NaCl	.3963	.076	126.42
KCl	.4906	.006	149.82
HCl	.8210	−.054	426.04

Values of T_+ computed by means of (4) and the data of Table VIII are compared with the observed values in Table IX. The deviations between observed and computed values are neither systematic nor large and Equation (4) can therefore safely be used for interpolation to 0.1 normal and for extrapolation to lower concentrations. Values computed by means of Equation (4) for round concentrations except the values for 0.2 N are summarized in Table X. In cases where the last figure appears in smaller type, that figure may be in error ±3 units, except for the data on potassium chloride below 0.005 N, where the error may be slightly greater.

TABLE IX

COMPARISON OF CALCULATED AND OBSERVED VALUES FOR T_+

Concn.	T_+ calcd.	T_+ obs.	$\Delta \times 10^4$	Concn.	T_+ calcd.	T_+ obs.	$\Delta \times 10^4$
	LiCl				KCl		
0.0098356	0.3290	0.3291	+1	0.001	0.4905	0.490_3	−2
.011104	.3286	.3287	+1	.002	.4904	$.490_3$	−1
.018515	.3264	.3264	0	.005	.4904	$.490_5$	+1
.032550	.3236	.3234	−2	.01	.4903	.4902	−1
.049942	.3211	.3210	−1	.02	.4901	.4901	0
.064021	.3196	.3198	+2	.05	.4899	.4900	+1
.10000	.3168	.3167	−1	.1	.4898	.4898	0
	NaCl				HCl		
0.01	0.3918	0.3919	+1	0.01	0.8251	0.8252	+1
.02	.3902	.3900	−2	.02	.8266	.8264	−2
.05	.3876	.3878	+2	.05	.8292	.8292	0
.1	.3854	.3853	−1	.1	.8314	.8314	0

[25] Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

The results are presented graphically in Fig. 4. In this figure the circles represent the experimental points and the smooth curves are the values computed from Equation (4) and the constants of Table VIII.

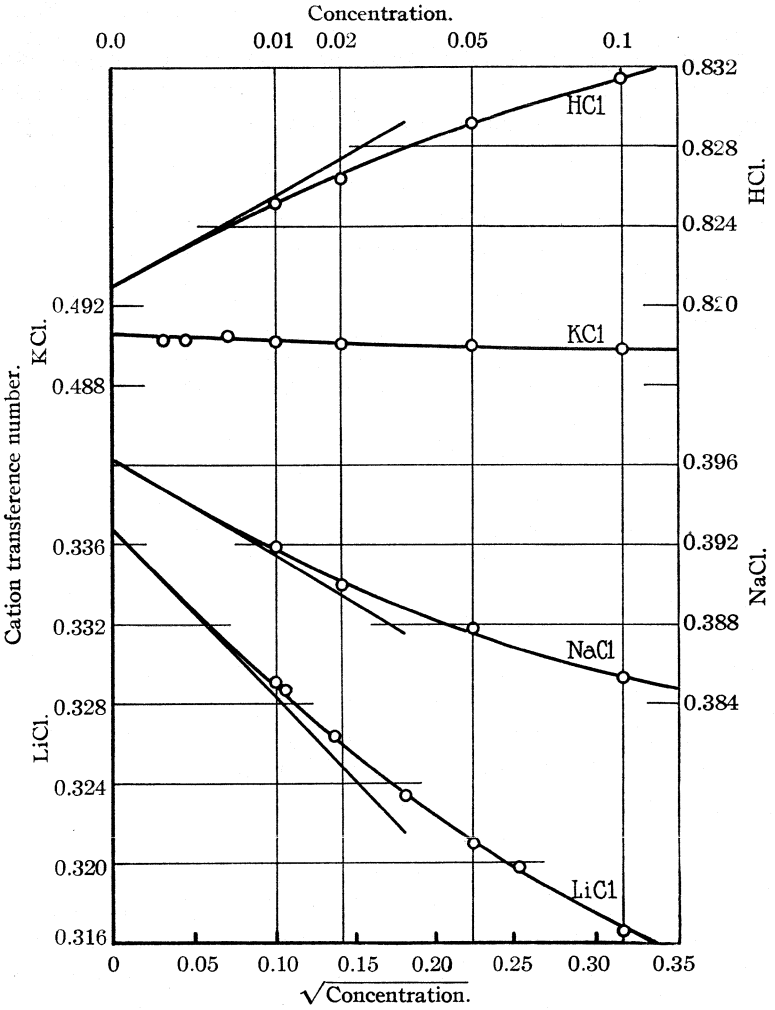


Fig. 4.—Graphical presentation of data showing approach to theoretical limiting slope. Circles represent experimental points; smooth curve represents values computed by Equation (4).

The curves through the experimental points are evidently approaching the limiting slopes which are represented in the figure by the straight full lines. In the case of potassium chloride the limiting slope and the curve given by Equation (4) are nearly coincident up to a concentration of several hundredths normal.

In conclusion the author would like to express his sincere appreciation to Dr. D. A. MacInnes for many suggestions during the course of this work and for valuable criticism during the preparation of this paper.

Summary

Measurements of the transference numbers at 25° of aqueous solutions of potassium chloride, sodium chloride, lithium chloride and hydrochloric acid by the moving boundary method have been made. The results are given in Table X.

TABLE X

TRANSFERENCE NUMBERS AT 25° OF POTASSIUM CHLORIDE, SODIUM CHLORIDE, LITHIUM CHLORIDE AND HYDROCHLORIC ACID

Concn.	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
KCl	$.490_5$	$.490_4$	$.490_4$	.4903	.4901	.4899	.4898	$.489_2$
NaCl	...	...	...	.3918	.3902	.3876	.3854	$.381_4$
HCl	...	...	...	$.825_1$	$.826_6$	$.829_2$	$.831_4$	...
LiCl	...	...	...	.3289	.3261	.3211	.3168	...

A correction for the conductance of the solvent, neglected by previous workers, has been found to be important when dilute solutions are measured.

An equation connecting the transference numbers with the concentration, which is useful for interpolation, and which gives a correct extrapolation to infinite dilution, is given.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE LIMITING EQUIVALENT CONDUCTANCES OF SEVERAL UNIVALENT IONS IN WATER AT 25°

BY DUNCAN A. MACINNES, THEODORE SHEDLOVSKY AND LEWIS G. LONGSWORTH

RECEIVED MARCH 17, 1932 PUBLISHED JULY 6, 1932

Data on the conductances of aqueous solutions of a number of binary electrolytes at concentrations ranging from 3×10^{-5} to 0.1 N are given in recent papers from this Laboratory,[1] and an article preceding this one describes the accurate determination of the transference numbers of four chlorides in the range 0.01 to 0.1 N.[2] With these data at hand we have been able to arrive at some definite conclusions concerning the equivalent conductances of ion constituents, and the values of the limiting ion mobilities.

Table I contains the assembled data on the equivalent conductances, Λ, of four chlorides and the corresponding transference numbers of the

[1] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[2] Longsworth, *ibid.*, **54**, 2741 (1932).

chloride ion, T_{Cl}. These transference numbers are the directly determined values with the exception of those for lithium chloride, which have been brought to round concentrations by very short interpolations. From these data the equivalent conductances of the chloride ion constituents have been computed, and the results have been tabulated in the fourth column of the table.

TABLE I

EQUIVALENT CONDUCTANCES OF CHLORIDE ION CONSTITUENTS AT 25°

Concn.	Equivalent cond., Λ	Trans. no., T_{Cl}	Cond. of chloride ion constituent, $T_{Cl}\,\Lambda = \lambda_{Cl}$ Observed	Computed
		KCl		
0.01	141.32	0.5098	72.04	72.04
.02	138.34	.5099	70.54	70.54
.05	133.33	.5100	68.00	67.99
.10	128.90	.5102	65.76	65.76
		NaCl		
0.01	118.43	0.6081	72.01	72.03
.02	115.65	.6100	70.54	70.51
.05	110.88	.6122	67.88	67.89
.10	106.68	.6147	65.57	65.56
		HCl		
0.01	411.88	0.1748	71.99	72.08
.02	407.12	.1736	70.67	70.59
.05	398.97	.1708	68.14	68.11
.10	391.20	.1686	65.96	65.98
		LiCl		
0.01	107.29	0.6711	72.00	72.04
.02	104.62	.6739	70.50	70.51
.05	100.08	.6789	67.94	67.85
.10	95.83	.6832	65.47	65.48

If values of λ_{Cl} for the four chlorides at equivalent concentrations are compared it will be seen that they are very nearly the same at 0.01 and 0.02 *N* but show definite deviations from each other at 0.05 and 0.1 *N*. This is not in accord with the observations of Lewis[3] and MacInnes,[4] who found from less accurate data that the chloride ion conductance appeared to be independent of its univalent co-ion up to a concentration of 0.1 *N*.

The data in Table I may be used to discover how the conductance of the chloride ion constituent changes with the concentration. Shedlovsky[5] has proposed an empirical extension of Onsager's equation for the change of the equivalent conductance of a uni-univalent electrolyte with the concentration, *C*, having the form

[3] G. N. Lewis, THIS JOURNAL, **34**, 1631 (1912).

[4] MacInnes, *ibid.*, **43**, 1217 (1921).

[5] Shedlovsky, *ibid.*, **54**, 1405 (1932).

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} - BC \qquad (1)$$

With a few exceptions this equation has been found to hold with high accuracy for uni-univalent electrolytes up to 0.1 *N*.

In Onsager's equation

$$\alpha = \frac{5.78 \times 10^{-5}}{(DT)^{3/2}} \text{ and } \beta = \frac{58.0\sqrt{2}}{\eta(DT)^{3/2}}$$

in which D is the dielectric constant, T the absolute temperature, and η the viscosity. The numerical coefficients depend upon universal constants. The extension of Onsager's equation consists of the term BC in which B is an empirical constant. For the equivalent conductance of an ion constituent $\lambda = T\Lambda$ the corresponding equation is

$$\lambda_0 = \frac{\lambda + 1/2\,\beta\sqrt{C}}{1 - \alpha\sqrt{C}} - bC \qquad (2)$$

in which λ_0 is the limiting equivalent conductance of the ion species and b is an empirical constant.

To use Equation (2) it is convenient to compute values of

$$\frac{\lambda + 1/2\,\beta\sqrt{C}}{1 - \alpha\sqrt{C}} = \lambda_0' \qquad (3)$$

and plot them against C. Figure 1 shows values of λ_0' for the chloride ion constituent plotted in this way. The result is a straight line for

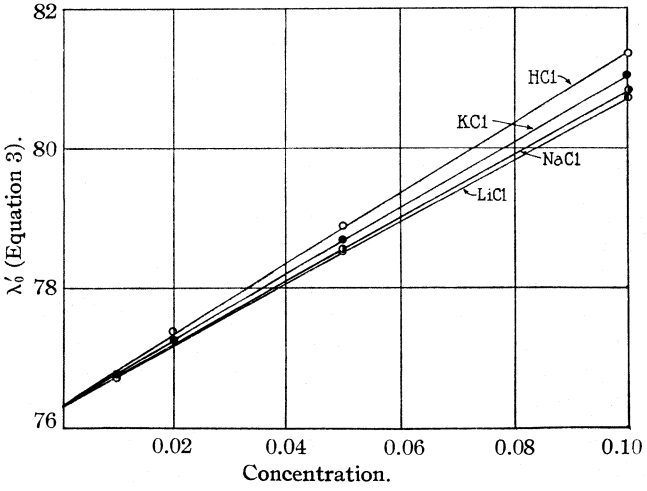


Fig. 1.

the λ_0' values from each of the electrolytes. The four lines converge and meet at a point at zero concentration. Equation (2) thus provides a method for obtaining the limiting conductance of the chloride ion, λ_{0Cl}.

The most probable values of that constant and of b for each electrolyte were found by applying the method of least squares to the equation

$$\lambda_0' = \lambda_0 + bC$$

The resulting constants are given in Table II.

TABLE II

COMPUTED VALUES OF THE LIMITING CONDUCTANCE AT 25° OF THE CHLORIDE ION

Substance	b	λ_0 for Cl ion
KCl	47.30	76.31
NaCl	45.00	76.32
LiCl	44.09	76.34
HCl	49.50	76.32
	Average	76.32

It will be observed that the values for the limiting chloride ion conductance thus obtained are, within about 0.02%, the same from all four chlorides. The close agreement of the data with Equation (1) is best shown by comparing in Table I the observed and computed values of λ_{Cl}, the latter having been obtained by using in that equation the appropriate values of the constants in Table II. The comparatively large difference between the computed and measured values for 0.05 N for lithium chloride possibly indicates that the behavior of this substance may be influenced by some secondary effect, particularly as the conductance values of this salt deviate from Shedlovsky's equation at a lower concentration than is observed for the other electrolytes under consideration. However, the agreement shows that Equation (2) for the chloride ion constituent holds as well as Equation (1) has been found to do for complete uni-univalent electrolytes.

A check on the mean value of λ_{0Cl} in Table II is given by the limiting conductance value for potassium chloride, $\Lambda_0 = 149.82$, obtained by Shedlovsky from his measurements on the most dilute solutions, and the limiting value of the transference number, $T_{0Cl} = 0.5094$, of that salt, as given by Longsworth in the paper preceding this one. The product of these two figures yields $\lambda_{0Cl} = 76.32$, agreeing exactly with the average value by the other method. Using the data from say 3×10^{-5} to 0.001 N an accurate extrapolation may be made of the conductance data by simply plotting the equivalent conductance values against the square root of the concentration. This does not involve the extension of the Onsager equation. The very close agreements just shown may be in some measure fortuitous, particularly as the transference numbers at the lower concentrations are not known to this high degree of accuracy.

It will be noted that the value $\lambda_{0Cl} = 76.32$ differs quite widely from that generally accepted for this constant. Noyes and Falk[6] give $\lambda_{0Cl} = 75.8$

[6] Noyes and Falk, THIS JOURNAL, **34**, 454 (1912).

and the figures in the "International Critical Tables"[7] yield 75.1 if the value at 18° and the temperature coefficient there given are used. It is important to note that *the new value of the constant is not dependent on any one transference number as were the older figures, the same value within a very narrow range being obtained from data on four electrolytes and four series of determinations of transference numbers.*

From the λ_{0Cl} value just given and the limiting conductances, Λ_0, from the recent papers by Shedlovsky and MacInnes and Shedlovsky,[1] the limiting ion conductances of a number of ions may be computed from Kohlrausch's law of independent ion mobilities. The results, which are collected in Table III, are all on the basis that a "demal" solution of potassium chloride, containing 7.47896 g. of potassium chloride and 1000 g. of water (weighed in air) has a specific conductance value of 0.012852_4 at 25°.[8]

TABLE III

LIMITING ION CONDUCTANCES AT 25°

Cations		Anions	
K^+	73.50	Cl^-	76.32
Na^+	50.10	NO_3^-	71.42
H^+	349.72	CH_3COO^-	40.87
Ag^+	61.90		
Li^+	38.68		

These constants will be added to from time to time as the work in this Laboratory proceeds. A more elaborate theoretical discussion of the results will also be given along with further data, some of which are already at hand.

Summary

A table is given of the limiting conductance at 25° of eight ion species, based on transference and conductance values obtained in this Laboratory. The extrapolations have been made with an extension of Onsager's equation, which reduces to that equation in the limit. Closely agreeing values of the limiting chloride ion conductance have been found from the use of conductance and transference data on four different chlorides.

NEW YORK, N. Y.

[7] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 230.

[8] Parker and Parker, THIS JOURNAL, **46**, 332 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

ACTIVITY COEFFICIENTS OF SULFURIC ACID IN ANHYDROUS ACETIC ACID

BY VICTOR K. LA MER AND W. C. EICHELBERGER[1]

RECEIVED MARCH 30, 1932 PUBLISHED JULY 6, 1932

In a recent paper Hutchison and Chandlee[2] have reported measurements on the cell without transfer

$$H_2,\ H_2SO_4 \text{ in glacial acetic acid},\ Hg_2SO_4,\ Hg \qquad (1)$$

corresponding to the process $H_2(g) + Hg_2SO_4(s) = H_2SO_4(m) + 2Hg(l)$ (2 faradays) at 25° for molalities of sulfuric acid ranging from $m = 0.8715$ to $m = 0.0025$. These measurements are particularly valuable for, as the authors point out, they are not burdened with the uncertainties of liquid junction potentials, and the logical objections to individual ion activities which are inherent in data obtained from cells with transference, a criticism that may be raised against previous e. m. f. measurements in glacial acetic acid.

In this paper we shall present a modified interpretation of their data and show that they conform to the Debye–Hückel theory over a wider concentration range than does the original interpretation.

To evaluate $E°$, for the computation of the mean activity coefficients of sulfuric acid, Hutchison and Chandlee consider sulfuric acid as a ternary electrolyte ($\nu = 3$) dissociating into 2 H^+ and $SO_4^=$ ions, and employ a two parameter equation; namely, the simple form of the Debye–Hückel theory (first approximation of the Poisson–Boltzmann equation) in combination with the linear term added by Hückel to account for changes in the dielectric constant, as a control on the extrapolation to infinite dilution. Since the dielectric constants of conducting solutions are not susceptible to experimental measurement and in aqueous solutions where the various attempts at measurement have led to widely different and often absurd results,[3] the arbitrary parameter B involved in the Hückel extension cannot be regarded at the present time other than as a purely empirical correction term, we shall therefore restrict our computations to the region where the better theoretically founded parameter "a," corresponding to the distance of closest approach of the ions, involved in the original form of the theory suffices as an explanation.

Our treatment differs in that we shall consider sulfuric acid when dissolved in glacial acetic acid as a binary electrolyte ($\nu = 2$) dissociating into H^+ and HSO_4^- ions. Owing to the high degree of acidity of glacial acetic acid, any secondary dissociation of the HSO_4^- ion into SO_4^{--} and

[1] National Research Council Fellow.

[2] Hutchison and Chandlee, THIS JOURNAL, **53**, 2881 (1931).

[3] Harned, *ibid.*, **48**, 326 (1926).

H^+ ions would be completely repressed. In addition we shall take into account the higher terms, (III) and (V), of the Gronwall, La Mer and Sandved[4] solution of the Poisson–Boltzmann equation which were neglected in Hutchison and Chandlee's treatment, namely

$$-\log_{10} f = 19.63 \left(\frac{z^2}{a}\right) \underbrace{\frac{x}{1+x}}_{\text{(I)}} - 320.7 \left(\frac{z^2}{a}\right)^3 \cdot 10^3 \underbrace{\left[\frac{1}{2} X_3(x) - 2Y_3(x)\right]}_{\text{III}}$$
$$-26{,}200 \left(\frac{z^2}{a}\right)^5 \cdot 10^5 \underbrace{\left[\frac{1}{2} X_5(x) - 4Y_5(x)\right]}_{\text{V}} \qquad (2)$$

In Table I are given the observed e. m. f.'s, E, corresponding to the molalities m. The other quantities are defined as follows

$$E^{\circ\prime} = E + \frac{\nu RT}{nF} \log m = E + 0.05915 \log m$$
$$= E^\circ - 0.05915 \log f \qquad (3)$$
$$\kappa = \sqrt{\frac{4\pi N\epsilon^2}{1000\, kTD} \sum n_j z_j^2} = 1.1734 \times 10^8 \sqrt{c} \qquad (4)$$

when we substitute D (acetic acid) = 6.165 and the numerical values of the universal constants. It is important to emphasize that the assump-

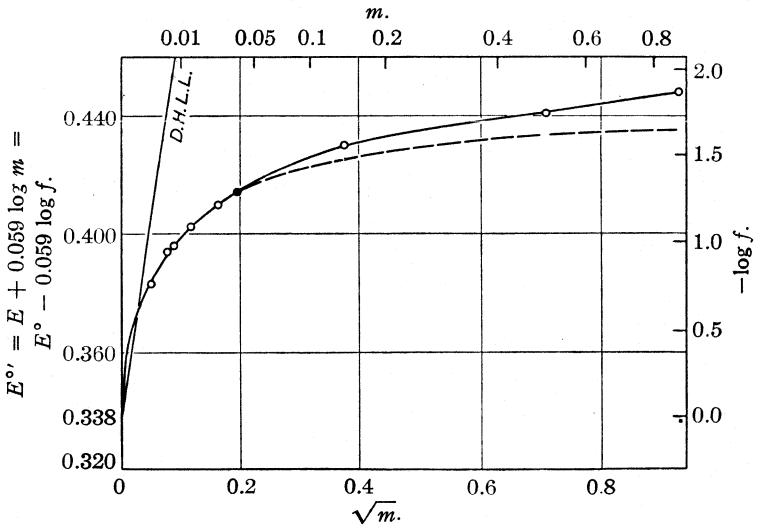


Fig. 1.—Heavy curve—Experimental: $E^{\circ\prime} = E + 0.05915 \log m$. Dotted curve—Theory: Gronwall, La Mer and Sandved; "a" = 11 Å.; $E^{\circ\prime} = E^\circ - 0.05915 \log f = 0.338 + 0.05915$ [Eq. (2)].

tion that $\nu = 2$ leads to an entirely different set of values for $E^{\circ\prime}$ and consequently for E° than those employed by Hutchison and Chandlee. Similarly, their values of κ are reduced by the factor $\sqrt{3}$ and the limiting

[4] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

slope of $\log f$ against $\sqrt{m}$ by the factor $2\sqrt{3}$ by this assumption. Another advantage is that we can employ the symmetrical solution of the Poisson–Boltzmann equation as given by Gronwall, La Mer and Sandved[4] and not be obliged to carry out the tedious computations involved in the unsymmetrical case.[5]

TABLE I

COMPUTATION OF $E^{\circ\prime}$ FOR $\nu = 2$

No.	m	E	$E^{\circ\prime}$	c	$\sqrt{c}$	$10^{-3}\kappa$
1	0.002461	0.537	0.3827	0.002567	0.05067	0.0595
2	.006053	.525	$.3938$	.006315	.07947	.0933
3	.007730	.521	$.3961$	.008063	.08979	.1054
4	.01377	.512	$.4019$	.01436	.1198	.1406
5	.02662	.5035	$.4104$	.02773	.1665	.1954
6	.03796	.498	$.4140$	.03954	.1988	.2333
7	.1437	.480	$.4302$	.1490	.3860	.4529
8	.5014	.459	$.4413$	.5133	.7164	.8406
9	.8715	.452	$.4485$	.8770	.9365	1.0989

Table II gives the computations for "a" = 11 Å., which value of "a" gives the most constant and therefore the most acceptable value of E°.[6] The computed values of E° for this and other values of "a" are plotted in Fig. 2. It is noteworthy that a one-parameter function yields a value of E° which is constant to within the limits of experimental error (± 0.001 volt) for the six determinations extending over the concentration range $m = 0.0025$ to $m = 0.038$, whereas under the assumption $\nu = 3$ two parameters are required to account for these data. A small empirical correction term of the order of $0.02\,m$ is sufficient to account for the deviation of the last three points from $E^{\circ} = 0.338$.

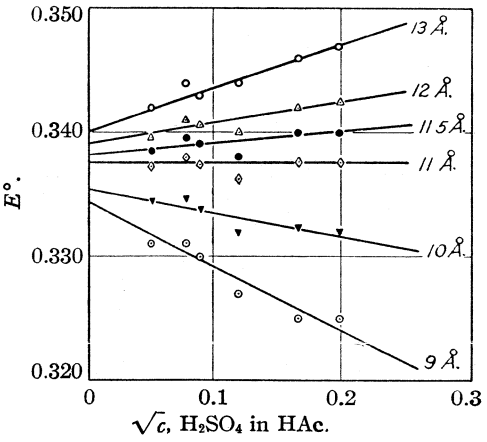


Fig. 2.

From recent measurements on the solubility of univalent salts in glacial acetic acid, Seward and Hamblet[7] have shown that "a" is equal to 8.5 to 9.5 Å. and that it is unnecessary in dilute solution to introduce a term for change of dielectric constant, which is in agreement with our conclusions.

[5] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

[6] For details concerning this computation see La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931); Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[7] Seward and Hamblet, *ibid.*, **54**, 554 (1932).

TABLE II

COMPUTATION OF E° FOR "a" = 11 Å.

No.	$x = \kappa a$	I	III	V	$-\log f$	$-0.05915 \log f$	E°
1	0.6541	+0.706	−0.088	+0.026	+0.768	0.0454	0.337
2	1.0258	.904	− .057	.018	.943	.0558	.338
3	1.1594	.958	− .048	.014	.992	.0587	.337
4	1.5466	1.084	− .028	.003	1.109	.0656	.336
5	2.1494	1.218	− .013	..	1.231	.0728	.338
6	2.5663	1.284	− .007	..	1.291	.0764	.338
7	4.9819	1.487	.....	..	1.487	.0880	.342
8	9.2466	1.611	.....	..	1.611	.0953	.346
9	12.0879	1.649	.....	..	1.469	.0975	.351

Summary

The e. m. f. measurements of Hutchison and Chandlee on the activity coefficient of sulfuric acid in glacial acetic acid can be accounted for on the basis of the Gronwall, La Mer and Sandved extension of the Debye–Hückel theory on the assumption that sulfuric acid behaves as a binary electrolyte in this solvent with an "a" value equal to 11 Å., for the concentration range $m = 0.0025$ to 0.038.

$E^\circ = 0.338$ volt for the cell H_2, H_2SO_4 in glacial acetic acid, Hg_2SO_4, Hg.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE, AND THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

MOLECULAR ROTATION IN THE SOLID STATE. THE VARIATION OF THE CRYSTAL STRUCTURE OF AMMONIUM NITRATE WITH TEMPERATURE

BY S. B. HENDRICKS, E. POSNJAK AND F. C. KRACEK

RECEIVED APRIL 4, 1932 PUBLISHED JULY 6, 1932

The phenomenon of molecular rotation in the solid state, first recognized by L. Pauling,[1] is proving of wide occurrence. In sodium nitrate[2] the picking up of rotational energy by the nitrate groups takes place over an extended temperature interval and is accompanied by *gradual* changes in such properties as coherent scattering of x-rays, heat capacity and specific volume. Pauling interpreted the *gradual* transitions shown by methane, hydrogen bromide, hydrogen iodide and the ammonium halides as accompanying molecular rotation. He also suggested that the *polymorphic* transitions shown by nitrogen (35.4°K.), oxygen (43.75°K.) and hydrogen chloride (93.36°K.) are accompanied by the excitation of molecular rotation.

The several gradual transitions shown by hydrogen bromide and hydro-

[1] L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

[2] F. C. Kracek, E. Posnjak, S. B. Hendricks, THIS JOURNAL, **53**, 3339 (1931).

gen iodide[3] were supposed by Pauling to be connected with incipient rotation about various directions in the crystals. x-Ray powder diffraction photographs, recently obtained, from the various crystalline modifications of these compounds are not readily interpretable.[4] They are, however, in no sense incompatible with the concept of molecular rotation.

We have been fortunate in discovering in ammonium nitrate formal proof for the concept of molecular rotation in the solid state and evidence for the setting in of the rotation at a *polymorphic* transition point. The structures of the many modifications of ammonium nitrate have been studied in detail.

I. The Polymorphism of Ammonium Nitrate

Ammonium nitrate has one high pressure and five low pressure crystalline modifications. The inversion temperatures, the volume changes, and the latent heats of inversion have been determined;[5] the most probable values of these constants are given in the following tabulation.

Phase reaction	Temp., °C.	Volume change, cc./g.	Heat of inversion, cal./g.	Authors
I ⟷ II	125.2	0.013	11.9	Early and Lowry, Bellati and Finazzi, Bellati and Romanese, Behn
II ⟷ III	84.2	−.008	5.3	Early and Lowry, Bellati and Romanese, Behn
III ⟷ IV	32.3	.0221	4.99	Cohen and Kooy, Cohen and Heldeman
IV ⟷ V	−18	−.016	1.6	Behn
		−.018		
II ⟷ IV	45 to 51	...	..	Bowen, Behn

Three series of measurements of the relative dilatation of ammonium nitrate have been published, by Bellati and Romanese, Bellati and Finazzi, and U. Behn. These series are not in mutual agreement because of errors in the elimination of the expansion of the dilatometer liquid. We have recalculated the results employing the accurate values of specific volumes at 32.0 and 32.5° for modifications IV and III by Cohen and Kooy, and the density 1.725 *ca.* 18° (Behn, Retgers).[6] The recalculated results are represented in Fig. 1.

[3] W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 2198 (1928); **51**, 1441 (1929).

[4] B. Ruhemann and F. Simon, *Z. physik. Chem.*, **15**, 389 (1932). See also G. Natta, *Nature*, **127**, 235 (1931).

[5] "International Critical Tables," Vol. IV, p. 7; P. Groth, *Chem. Krystallographie*, Leipzig, Vol. 2; Bellati and Finazzi, *Atti ist. Veneto*, **69**, 1151 (1909); U. Behn, *Proc. Roy. Soc.* (London), **A80**, 444 (1908); Cohen and Kooy, *Z. physik. Chem.*, **109**, 81 (1924); Cohen and Helderman, *ibid.*, **113**, 145 (1924); N. L. Bowen, *J. Phys. Chem.*, **30**, 721 (1926).

[6] Other values quoted in the literature are largely accidental; thus Schröder is quoted as having determined $\rho = 1.737$, the actually measured values being 1.681 and 1.791. Many other determinations are vitiated by lack of physical homogeneity of the salt used.

The crystallographic observations on the various modifications indicate that ammonium nitrate is (I) cubic (optically isotropic) above 125°, (II) tetragonal (Wallerant) or trigonal (Lehmann, Gossner) between 125 and 84°, (III) orthorhombic (Lehman) or monoclinic pseudo-tetragonal (Wallerant) between 84 and 32°, (IV) orthorhombic pseudo-tetragonal (Wallerant) or orthorhombic pseudo-trigonal (Lehmann) between 32 and −18°, and (V) tetragonal below −18°. Only the room temperature orthorhombic modification (IV) has been measured crystallographically, with the result that two mutually incompatible sets of axial ratios have been published,

(a) 0.5834:1:0.736 (Retgers, Wallerant, based on measurements by Marignac)
(b) 0.9092:1:1.0553 (Gossner)

The latter set of axial ratios (b) agrees with our structural determinations.

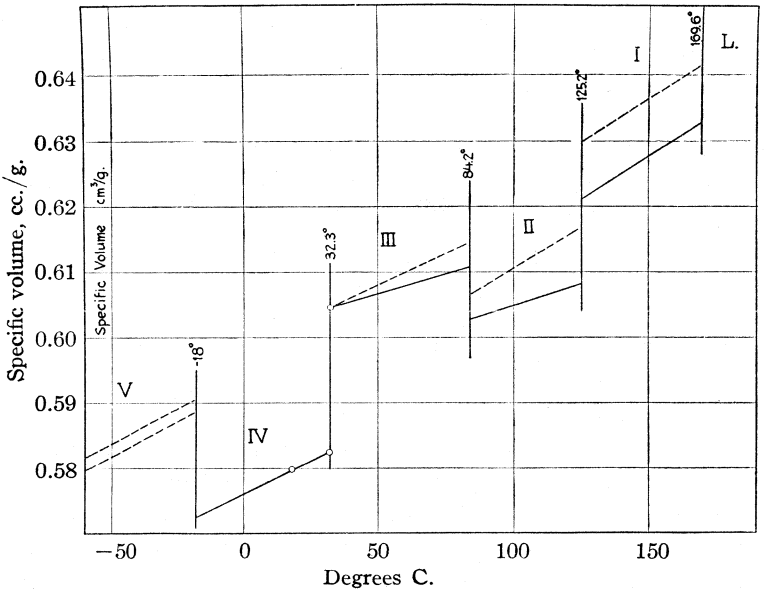


Fig. 1.—The specific volumes of the various modifications of ammonium nitrate. Circles represent the accurate values by Cohen and Kooy, and by Retgers. Full lines from relative expansion curves by Bellati and Romanese and Finazzi; broken lines, from relative expansion curves by Behn.

Bowen (1926) agrees with Wallerant that the 84 to 125° modification (II) is tetragonal, optically uniaxial and positive. He describes the 32 to 84° modification (III) as orthorhombic or monoclinic (optically biaxial), optic axial angle ($2V$) nearly 90°, with a moderately high birefringence, in comparison with the orthorhombic room temperature (IV) modification which has a very high birefringence, optic axial angle $2V$ about 35°.

We have studied the behavior of ammonium nitrate with the petro-

graphic microscope equipped with a heating stage. For reading the temperatures the stage is provided with a gold palladium–platinum rhodium thermocouple. The samples were prepared in the usual way, by melting a small quantity of the salt on an ordinary microscope slide, a cover-glass being then pressed down lightly to obtain a thin section. The lag in the inversions was clearly noticeable; the greatest lag is observed with the IV $\rightleftharpoons$ III inversion, which started at 36 to 40° with rising temperature, and 28 to 25° with falling temperature. When both phases are initially present, the lag is very much less; the boundary can then be seen to move quite rapidly at 33° in one direction and at 31 to 32° in the other. On raising the temperature to the III $\rightleftharpoons$ II inversion, the transformation starts quite promptly at about 85°. If the cooling is begun now before the temperature of the salt reaches 125°, modification II reverts to III directly, starting usually near 80°, but sometimes not until a temperature of 70 or even 65° is reached. If, on the other hand, the temperature is allowed to rise above the II $\rightleftharpoons$ I inversion near 125°, then, on subsequent cooling, the form II does not invert directly back to III as above, but it persists down to 48 or 45°, when it changes apparently to form IV, as also described by Bowen (*op. cit.*, p. 723). If the slide is very thin, and the salt well dried, the transformation is very like a single crystal to single crystal transition, taking place very rapidly, with barely a noticeable change in orientation and birefringence. If the slide is a little thicker than before, or the salt not too thoroughly dried, the transformation proceeds by recrystallization. If the temperature is allowed to decrease further, no other transformation occurs, either with the thin or the thick preparations, down to 0°. On heating now, the thin slides always revert back to form II at about 50 to 52°, again very rapidly, with a hardly noticeable change in birefringence. This metastable inversion can be carried back and forth in the thin films almost indefinitely, the metastable condition persisting for many hours; it is, however, rapidly destroyed by moisture. In the thicker slides the metastable inversion can sometimes also be reversed a number of times, but usually after three or four reversals the stable modification III appears. Sometimes this happens following the metastable inversion on cooling, as observed by Bowen, but often also on heating, and then only after the metastable inversion on heating has taken place. The difference in behavior of the very thin and the thicker slides at the metastable inversion is striking, as is likewise the reluctance of the preparations, when in the metastable condition, to assume the stable form.

II. The Crystal Structure of Ammonium Nitrate as a Function of Temperature

The Modification Stable between 125 and 169.5° (Melting Point, Cubic I).—x-Ray powder diffraction photographs were made with

MoK $\alpha_1\alpha_2$ radiation of a revolving sample of ammonium nitrate at 155°. The sample was obtained by cooling a melt. Photographs were also made with CuK $\alpha_1\alpha_2$ radiation of samples at 130–140°. In these cases the ammonium nitrate was ground finely and placed in small glass tubes which were rotated throughout the time of exposure. On account of the high rate of crystal growth it was necessary to change the sample every hour. The data obtained from these photographs are summarized in Table I.

TABLE I

POWDER PHOTOGRAPHIC DATA FROM CUBIC AMMONIUM NITRATE (I)

155° MoK $\alpha_1\alpha_2$ radiation (NaCl reference)

$\sin^2\Theta = 0.00648\,(h^2 + k^2 + l^2)$ $a_0 = 4.40$ Å.

Plane	$\sin^2\Theta$ (obs.)	$\sin^2\Theta$ (calcd.)	Int. obs.
(100)	0.00640	0.00648	v. s.
(110)	.01295	.01296	v. s.
(111)	.01955	.01944	w.
(200)	.0259	.0259	m.
(210)	.0321	.0324	v. w.
(211)	.0386	.0389	v. w.
(220)	.0522	.0518	v. w.
(300)(221)	.0588	.0583	w.
(310)	.0648	.0648	v. w.

The lattice required by these data is a simple cubic one. The unit of structure has $a_0 = 4.40$ Å. at 155°. The density calculated on the basis of such a unit containing $1NH_4NO_3$ is 1.55 g./cc. in agreement with the experimentally observed value 1.57 g./cc.

The only possible atomic positions are:

(a) 000 (b) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

(3a) $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$ (3b) $\frac{1}{2}00$; $0\frac{1}{2}0$; $00\frac{1}{2}$

Combinations of these positions lead to calculated intensities entirely out of agreement with the observed intensities. Moreover, but we must remark secondarily, such arrangements do not give nitrate groups. It is thus impossible, if the geometrical concepts of crystal symmetry are to be retained, for the oxygen atoms to be in fixed positions.

Several possible escapes from this conclusion might be considered. (*1*) *Is the Symmetry Less than Cubic?*—The powder diffraction data would require the crystal axes to be approximately orthogonal and of equal lengths. The instance of $LiCl\cdot H_2O$ might be recalled as an illustration. H. Ott[7] from powder photographic data concluded that the structure of $LiCl\cdot H_2O$ was based upon a simple cubic lattice and that the unit of structure contains $1LiCl\cdot H_2O$. Since it is not possible to have three dissimilar atoms in such a unit he suggested that two of the atoms were associated, this pseudo atom being the one defined by the geometrical criteria. These observations, however, were inconsistent with the high birefringence and

[7] Ott, *Z. Krist.*, **63**, 231 (1926).

uniaxial character of $LiCl \cdot H_2O$. A closer examination[8] of the structure showed it to be tetragonal with an axial ratio of approximately unity. If the symmetry of ammonium nitrate were less than cubic and the unit of structure contained $1NH_4NO_3$, the birefringence would necessarily be high, as it is observed to be in the four modifications of ammonium nitrate stable below 125°, since the molecular birefringence of the nitrate group is high. It is thus improbable that the symmetry is less than cubic.

(2) *Is the Unit of Structure Larger?*—This would be possible if the atoms in question, oxygen atoms, had negligible F values in comparison with the other atoms in the compound. In ammonium nitrate the oxygen atoms are in no sense negligible, and there is no evidence for reflections other than the ones listed in Table I.

(3) *Molecular Rotation.*—Randomness in positions of the oxygen atoms may be interpreted as evidence for rotation of the nitrate groups. In order to calculate intensities of reflection it is necessary, on the basis of such data, to assume certain types of distributions. Several distributions were tried. The centers of the ammonium groups can be taken at 000, of the NO_3 groups at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Structure factors are listed in Table II calculated on the basis of the following assumptions: (1) the centers of the oxygen atoms are assumed to be randomly arranged on a sphere of 1.25 Å. radius about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, all positions of the oxygen atoms being considered equally probable; (2) the nitrate groups are assumed to be rotating with constant angular velocity in three orthogonal planes. In each case, the values of the structure factors, which are only approximate, lead to calculated intensities on the basis of assumed F curves, which are still not in good agreement with

TABLE II

STRUCTURE FACTORS FOR VARIOUS PLANES OF CUBIC AMMONIUM NITRATE (I)

Plane			$\sqrt{S} = A$ ($B = 0$) (1)	(2)	No. of planes in form	Intensity observed
(100)	$1F_{NH_4}$	$-1F_{N\ of\ NO_3}$	$-1.7F_0$	$-1.5F_0$	6	s.
(110)	1	+1	+0.7	+0.7	12	v. s.
(111)	1	−1		0	8	w.
(200)	1	+1	+0.2	−0.2	6	m.
(210)	1	−1	+0.3	+0.5	24	v. w.
(211)	1	+1		−0.6	24	v. w.
(220)	1	+1	−1.0	−0.4	12	v. w.
(300)	1	−1	−0.9	0.4	6	w.
(221)	1	−1		0.4	24	
(310)	1	+1	+0.2	−0.3	24	v. w.

(1) Calculated for the nitrate groups rotating with constant angular velocities in three orthogonal planes normal to the cubic axes.

(2) These calculations are based upon the assumption that the nitrate groups are rotating with approximately spherical symmetry.

[8] S. B. Hendricks, *Z. Krist.*, **66**, 298 (1927).

the observed intensities. This lack of agreement is merely indicative of over-simplification in the assumed models. It is quite probable that the nitrate groups do not rotate with constant angular velocities and that they do not generate any simple geometrical figure. In any case, however, it should be pointed out that all reflections beyond (110) are characteristically weak. Either of the above cases qualitatively requires this. It can be seen that if the oxygen atoms approach such arrangements they will contribute partially out of phase for all reflections.

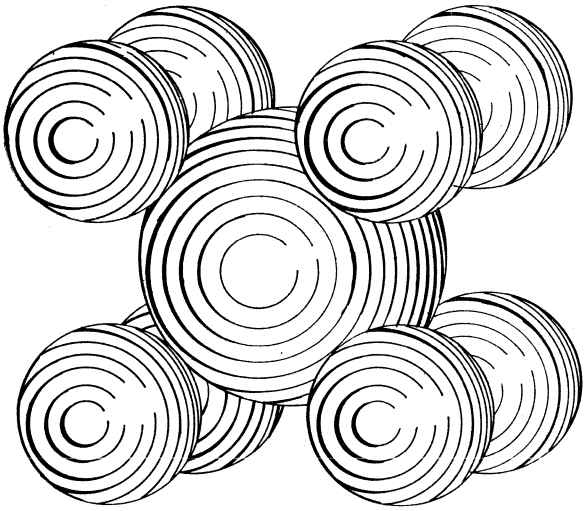


Fig. 2a.—Cubic ammonium nitrate (I). The small spheres represent ammonium groups, the large sphere a nitrate group rotating with spherical symmetry. a_0 = 4.40 Å. (155°).

One factor of importance to geometrical crystallography is brought into clear relief by this structure of ammonium nitrate. It would seem that the unit of structure is the smallest element that *statistically* has the symmetry of the crystal. If this is true the figure generated by a rotating nitrate group must have at least the symmetry of the point group T-23. The minimum symmetry might be that of any cubic point group, the actual that of a sphere.

The unit of structure with the rotating nitrate group represented as a spherical shell is shown in Fig. 2a. In Fig. 2b the nitrate group is represented as rotating in three orthogonal planes. If the angular velocity were constant, the symmetry of the generated figure would be that of the point group O_h—$4/m\ \bar{3}\ 2/m$. The minimum separation of points $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ is 4.40 Å., a_0. If the nitrogen to oxygen distances within the nitrate group are 1.25 Å., the oxygen ions would, in either case, approach within 1.90 Å. of one

another at some time *if the nitrate groups were rotating independently in phase.* This value is improbably small.[9]

Finally, it is interesting to note that ammonium chloride is soluble to the extent of *ca.* 8% by weight in cubic ammonium nitrate[10] and is not soluble, in detectable amounts, in the other crystalline modifications. If it is assumed that the ionic radius of NH_4^+ is 1.46 Å., the apparent radius of NO_3^- is 2.35 Å., in comparison with *ca.* 1.90 Å., the radius of Cl^- with a coördination number of eight. On this basis solid solution would be expected with the nitrate group acting as a structural unit (rotating).

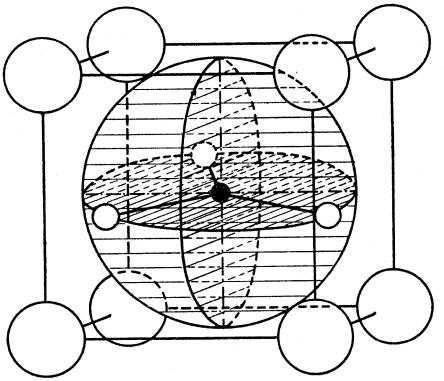


Fig. 2b.—Cubic ammonium nitrate (I). The structure is shown with the nitrate groups rotating in three orthogonal planes normal to the cubic axes. $a_0 = 4.40$ Å. (155°).

The Modification Stable between 125 and 84.2° (Tetragonal, II).—A number of powder photographs were made, with CuKα and MoKα radiation, from revolving samples of ammonium nitrate at 100 ± 10°. The samples were prepared and photographed as for the cubic modification. Some of the results obtained are summarized in Table III.

The data require a tetragonal unit of structure with a = b = 5.74 Å., c = 5.00 Å.

$$\text{CuK } \alpha_1 \sin^2\theta = 0.0181\,(h^2 + k^2) + 0.0236\,l^2$$
$$\text{MoK } \alpha_1 \sin^2\theta = 0.00380\,(h^2 + k^2) + 0.00501\,l^2$$

The density calculated on the basis of such a unit containing $2NH_4NO_3$ is 1.60 g./cc. in agreement with the observed value 1.64.

[9] Note for instance, W. H. Zachariasen, *Z. Krist.*, **80**, 137 (1931).

[10] N. L. Bowen, *J. Phys. Chem.*, **30**, 726 (1926).

TABLE III

POWDER PHOTOGRAPHIC DATA FROM TETRAGONAL AMMONIUM NITRATE (II)
100 ± 10°

Plane	Int.	MoK $\alpha_1\alpha_2$ radiation $\sin^2\theta$ calcd.	$\sin^2\theta$ obs.	Plane	Int.	MoK $\alpha_1\alpha_2$ radiation $\sin^2\theta$ calcd.	$\sin^2\theta$ obs.
(100)	a	0.00380	...	(201)	1	0.02021	0.0202
(001)	3	.00501	0.0047	(102)	a	.02384	...
(110)	7	.00760	.0074	(121)	3	.02401	.0238
(101)	a	.00881	...	(112)	1	.02764	.0280
(111)	10	.01261	.0125	(220)	2	.03040	.0303
(200)	6	.01520	.0150	(221)	0.5	.0354	.0361
(120)	3+	.01900	.0187	(113)	0.5+	.0527	.0539
(002)	a	.02004	...	(132)	0.5+	.0580	.0583

The presence of reflections from (001), (120), (111) and (112) and the assumptions that the nitrate group has approximately the same configuration as found in other nitrates and that two such groups, irrespective of orientation, must be separated by at least 2.6 Å. eliminate all space groups save

$$P4mm,\ P4bm,\ P4,\ P\bar{4}2_1m,\ P\bar{4},\ C\bar{4}2m$$

If it is assumed that the separation of the ammonium groups and of the ammonium and nitrate groups must be greater than 2.5 Å., that is, $\frac{1}{2}c$, the most general projection of the atomic arrangement on (001) is

$2NH_4$ at $00;\ \frac{1}{2}\frac{1}{2}$
$2N$ of NO_3 at $0\frac{1}{2};\ \frac{1}{2}0$
$2O$ at $0\frac{1}{2};\ \frac{1}{2}0$
$4O$ at $xy;\ \bar{x}\bar{y};\ \bar{y}x;\ y\bar{x}$

If it is assumed that the closest oxygen to oxygen distances in the nitrate groups are about 2.2 Å., then the intensities, as listed in Table IV, of $(hk0)$ require $x = 0.14$, $y = 0.36$, the values probably being accurate to ± 0.03. This might correspond to positions $u,\ \frac{1}{2} - u,\ v$, etc., with $u = 0.14$, arrangements derivable from space groups $P\bar{4}2_1m$, and $P4bm$. The paucity of the data does not permit the evaluation of the three or four parameters determining the atomic arrangement in the c direction. It might be stated, however, that an arrangement derivable from space group $P4-(C_4^1)$ seems to be required by the data.

TABLE IV

CALCULATED INTENSITIES FOR SOME $(hk0)$ OF TETRAGONAL AMMONIUM NITRATE (II)

Plane	Obs. int.	Intensity calculated $x = 0.31$ $y = 0$	$x = 0.33$ $y = 0.08$	$x = 0.35$ $y = 0.12$	$x = 0.36$ $y = 0.14$
(100)	a	1.7	0.7	0.1	0.0
(110)	7	1.6	1.8	2.0	1.8
(200)	6	6.7	5.5	4.5	4.0
(120) (210)	3+	1.6	2.4	2.7	2.8
(220)	2	0.2	1.1	1.9	2.1
(300)	a	1.2	0.3	0.0	0.0
(310) (130)	a	0	0.1	0.3	0.4

The projection of the atomic arrangement on (001), which is only approximate since x and y might be appreciably different from 0.14 and 0.36, respectively, is shown as Fig. 3. The nitrate groups probably are not rotating in this modification of ammonium nitrate.

It was very difficult to obtain reliable intensity measurements since the particle size increased rapidly at 100°. In particular on some films reflections from (110) and (220) were weak or absent. The absence of these reflections would be compatible with an entirely different type of structure that we have previously described in a letter to the Editor of *Nature*.[11] We are not certain at this time that these data are to be explained by crystal orientation.

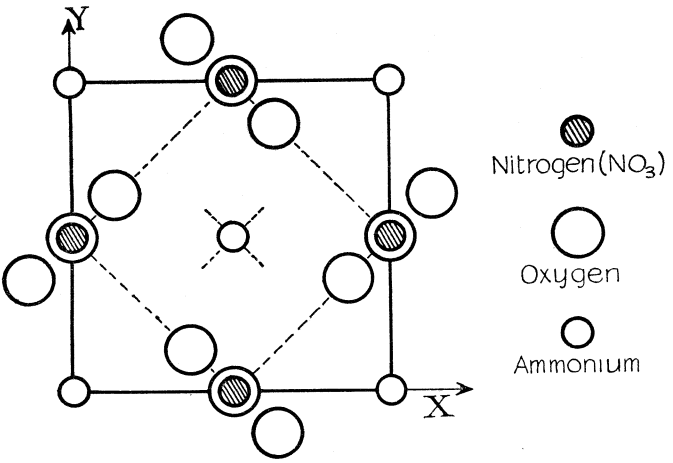


Fig. 3.—Tetragonal ammonium nitrate (II). Projection on (001).

In the microscopic work it was observed that the tetragonal modification II inverts directly to III, when it had originally been formed from III. On the other hand, if it had been formed from I by cooling from above 125°, it inverts metastably at 50° apparently to (IV) (orthorhombic room-temperature modification). It was also observed that the character of the metastable inversion depends on the specific experimental conditions of the sample, sometimes proceeding by distinct recrystallization with a high change in birefringence, at other times apparently as a single crystal transformation with practically no change in birefringence. This behavior might be due, partly or wholly, to the orientation of the crystals on the slide. The supposition suggests itself, however, that the character of the phases II and IV depends upon the previous thermal history of the salt such that II′ and IV′ closely similar to, but not identical with, II and IV, are formed under suitable conditions. Structures can be suggested

[11] F. C. Kracek, S. B. Hendricks and E. Posnjak, *Nature*, **128**, 410 (1931).

for hypothetical II′ and IV′ that would have optical properties identical with or closely similar to II and IV; these are not described since we have been unable to prove the existence of the hypothetical II′ and IV′.

The Modification Stable between 84.2 and 32.3° (Orthorhombic III).—Single crystals of this modification were prepared by slowly cooling saturated solutions of ammonium nitrate in absolute alcohol from 50 to 35°. The crystals were usually long needles often showing well-developed side faces. In all cases the angles between the only four developed side faces were 90°0′. Photographs were made with a crystal rotating about its needle axis and about axes normal to the needle axis. Weissenberg photographs were made of the equatorial zone in the former case. The room in which the photographs were made was maintained at a temperature greater than 35°. CuK radiation was used in all instances.

The Weissenberg photographs show two planes of symmetry at 90° to one another. Since the crystals are biaxial it follows that the symmetry is probably orthorhombic. This modification has previously been said to be monoclinic, by Wallerant.

The dimension of the unit of structure along the needle axis as determined from the layer line separations on the rotation photographs is

$$c = 5.80 \pm 0.05 \text{ Å}.$$

The other two dimensions of the unit of structure were determined from equatorial zone Weissenberg photographs about the c axis. They are

$$a = 7.06 \text{ Å}. \qquad b = 7.66 \text{ Å}.$$

These values are not particularly accurate since all reflections from (100) and (010) were quite weak and high orders were missing. The density calculated on the basis of such a unit of structure containing $4NH_4NO_3$ is 1.68 g./cc. in comparison with the observed value, 1.66.

The data obtained from Weissenberg and rotating crystal photographs are in part summarized in Tables V and VI. Planes of the type ($0kl$) with k odd and ($h0l$) with $(h + l)$ odd are observed to be characteristically absent in odd orders. All space groups requiring planes of other types to be absent are eliminated by the presence of observed reflections. These absences are consistent with the requirements of space group *Pbnm* (V_h^{16}). It should be borne in mind that there is no indication that the crystals are orthorhombic bipyramidal, and even if they were, space groups *Pmmm*, *Pmbm* and *Pnmm* could not be eliminated. The final justification for selecting space group *Pbnm* is that it leads to calculated intensities in agreement with the observed ones.

Possible atomic positions from *Pbnm* (V_h^{16}) are, in general

(a) $xyz;\ \bar{x},\bar{y},z+\frac{1}{2};\ \bar{x}+\frac{1}{2},y+\frac{1}{2},\bar{z}+\frac{1}{2};\ x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$
$\bar{x}\bar{y}\bar{z};\ x,y,\bar{z}+\frac{1}{2};\ x+\frac{1}{2},\bar{y}+\frac{1}{2},z+\frac{1}{2};\ \bar{x}+\frac{1}{2},y+\frac{1}{2},z$

on the reflection planes

(b) $uv\frac{1}{4};\ \bar{u}\bar{v}\frac{3}{4};\ \bar{u}+\frac{1}{2},v+\frac{1}{2},\frac{1}{4};\ u+\frac{1}{2}\bar{v},+\frac{1}{2},\frac{3}{4}$

without degrees of freedom, at symmetry centers

(c) $000; 00\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}\frac{1}{2}$
(d) $\frac{1}{2}00; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}$

If it is assumed that NO_3 groups are present in the structure, then the observations that the maximum axis of the optical ellipsoid is parallel to c and that the intensities of reflection from (001) are second order m, and fourth order m. s., require the ammonium ions to be on the reflection planes (b) and the oxygen ions to be at (a) and (b). The intensities of reflections from the two orders of (001) are compatible with $z = 0.06$, a value to be expected if the nitrate groups are stationary with a configuration similar to that found in other nitrates.

The parameters to be determined are

x,y for oxygen in the general positions
u_1,v_1, for oxygen on the reflection planes
u_2,v_2, for ammonium groups on the reflection planes
u_3,v_3, for nitrogen atoms, of NO_3 group, on the reflection planes.

In this place only an outline of the method used in the parameter determination can be given. In the first approximation the effect of the nitrogen atoms of the nitrate groups on the intensities of reflection can be neglected. The remaining six parameters, which in both instances can be evaluated owing to unusual combinations of data, are separable into two groups of three each. Since structure factors for even order reflections from (hkl) are of the type

$$A = 8F_0 \cos 2\pi n\,(hx) \cos 2\pi n\,(ky) \cos 2\pi n\,(lz) + 4\sum_{r=1}^{3} F_r \cos 2\pi n\,(hu_r) \cos 2\pi n(kv_r) \cos 2\pi n(l/4)$$

the observed absence or low intensities of reflections from (400) and (402) require x to be ± 0.07; $\pm(\frac{1}{4} \pm 0.07)$; $(\frac{1}{2} \pm 0.07)$ since $\cos 2\pi\,(4x)$ must be approximately zero.

The high value of the optic axial angle ($2V$ *ca.* 90°) clearly indicates that the planes of the nitrate groups are not approximately parallel to (010) or (100). This and the assumption that the NH_4–O distances must be greater than 2.5 Å. greatly facilitate the determination of the other two parameters in the a direction. In particular the observations

(400)a	(200)v. s.	(101)m. s.	(600)a
(402)a	(202)s	(303)m. s.	

limit u_1, u_2 and x to the following combinations

$u_1 = -0.32$	$u_1 = -0.18$	$u_1 = -0.32$	$u_1 = -0.18$
$u_2 = 0.18$	$u_2 = 0.18$	$u_2 = 0.32$	$u_2 = 0.32$
$x = -0.43$	$x = -0.07$	$x = -0.43$	$x = -0.07$

If it is now assumed that the nitrate groups have approximately the same configurations as found in other nitrates, then the above parameter limitations require $v_1 = y \pm 0.22$. The values of the two remaining parameters

y and v_2 can be determined from the intensities of reflections $(0kl)$ and (hkl) in combination with the above values. The final values are

$u_1 = -0.19$	$x = -0.07$	$v_3 = -0.19$
$u_2 = 0.30$	$v_1 = -0.05$	$y = -0.27$
$u_3 = -0.09$	$v_2 = 0.52$	$z = 0.06$

These values are probably accurate to ± 0.03.

TABLE V

WEISSENBERG PHOTOGRAPHIC DATA FROM ORTHORHOMBIC AMMONIUM NITRATE (III) ABOVE 32°

(001) Axis of rotation; equatorial zone; CuK radiation; temperature, 35°

	$h00$	$h10$	$h20$	$h30$	$h40$	$h50$	$h60$	$h80$
$0k0$			v. w.		m.		w.	w.
$1k0$		m.	m. s.	s.	a.	m. w.	a.	
$2k0$	v. w.	v. v. s.	s.	m. w.	a.	v. w.		
$3k0$		m. m. s.	m.	v. w.	m. m. s.	w.		
$4k0$	v. w.	m. m. s.	$w.^-$	w.—v. w.				
$5k0$		m.	$w.^+$					
$6k0$	v. w.							

The agreement between observed and calculated intensities of reflection is shown in Table VI. The intensities were calculated on the basis of the

TABLE VI

ROTATING CRYSTAL PHOTOGRAPHIC DATA FROM ORTHORHOMBIC AMMONIUM NITRATE (III) STABLE ABOVE 32°

(001) Axis of rotation; CuK α radiation; temperature, 35°

Equatorial zone			1st layer line			2d layer line			3d layer line		
Plane	Int. obs.	Int. calcd.	Plane	Int. obs.	Int. calcd.	Plane	Int. obs.	Int. calcd.	Plane	Int. obs.	Int. calcd.
(010)	a.	0	(011)	a.	0	(012)	a.	0			
(100)	a.	0	(101)	v. s.	4000	(102)	a.	0			
(110)	m.	550	(111)	s.	1300	(112)	s.	400			
(020)	a.	1	(021)	s.	70	(022)	v. s.	1250			
(200)	v. w.	8	(201)	a.	0	(202)	s.	750			
(120)	s.	370	(121)	m. s.	240	(122)	s.	280	(123)	a.	20
(210)	v. s.	3000	(211)	m. s.	15	(212)	w.	80	(213)	w.	25
(220)	s.	500	(221)	m. w.	30	(222)	w.	65	(223)	m. w.	22
(030)	a.	0	(031)	a.	0	(032)	a.	0	(033)	a.	0
(130)	s.	270	(131)		100	(132)	a.	10	(133)	m. s.	160
(300)	a.	0	(301)	m.	200	(302)	a.	0	(303)	m. s.	160
(310)	m.	10	(311)	a.	0	(312)	m. s.	280	(313)	m. s.	35
(230)	m. s.	140	(231)	w.	5	(232)	m.	100	(233)	v. w.	30
(320)	m.	90	(321)	m. s.—s.	130	(322)	m.	15	(323)	v. w.	30
(040)	m.	660	(041)	a.	20	(042)	a.	2	(043)	m. w.	10
(140)	a.	200	(141)	m.	4	(142)	m. w.	30	(143)	m.	40
(400)	a.	8	(401)	a.	0	(402)	a.	3	(403)	a.	0
(330)	v. w.	80	(331)	a.	37	(332)	a.	0	(333)	a.	25
(410)	s.	400	(411)	a.	7	(412)	s.	140	(413)	m.	90
(240)	a.	15	(241)	m. w.	70	(242)	m.	180	(243)	v. w.	33
(420)	a.	50	(421)	a.	2	(422)	a.	3	(423)	a.	2
(050)	a.	0	(051)	a.	0	(052)	a.	0	(053)	a.	0

F curves described in the next section. The agreement is only moderate but since the calculated intensities are sensitive to slight changes in parameter values no particular significance can be attached to the discrepancies observed.

The atomic arrangement is illustrated in Fig. 4, which is a projection on (001). The structure is hardly as simple as that of aragonite[12] or potassium nitrate[13] in which the planes of the NO_3 groups are parallel to one of the pinacoids.

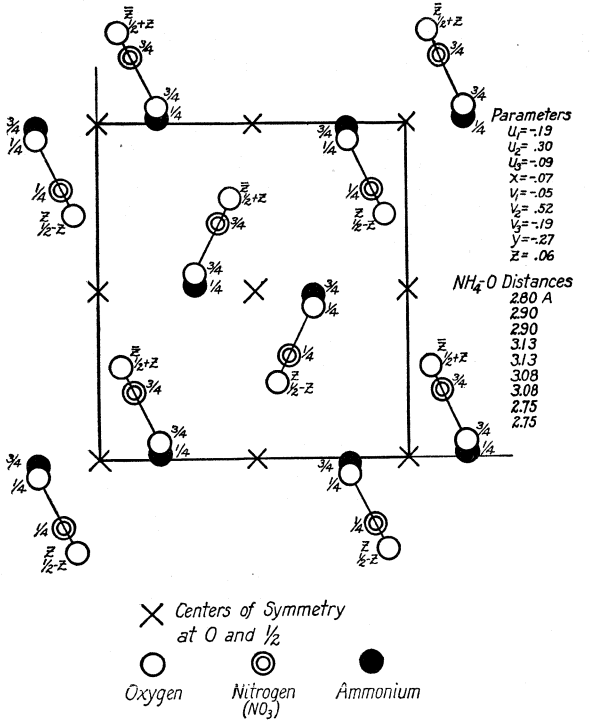


Fig. 4.—Orthorhombic ammonium nitrate (III) stable between 32.3 and 84.2°. Projection on (001) with distances above projection plane indicated.

An ammonium ion is approximately equidistant from nine oxygen ions. With the above parameter values these distances are: 2.75, 2.75, 2.80, 2.90, 2.90, 3.08, 3.08, 3.13, 3.13 Å. Each oxygen ion is approximately equidistant from three NH_4 groups.

An element of the structure in the c direction is shown as Fig. 5. This element is also to be found in the orthorhombic modification stable at room temperature. The dimension determined by it is 5.7–5.8 Å. This dimen-

[12] W. L. Bragg, *Proc. Roy. Soc.* (London), **A105**, 16 (1924).

[13] D. A. Edwards, *Z. Krist.*, **80**, 154 (1931).

sion is further found as $d_{(100)}$ for the tetragonal modification although it apparently is not determined by the same structural element.

The Modification Stable between 32.3 and −18° (Orthorhombic IV).—The modification of ammonium nitrate stable at room temperatures has been described as orthorhombic bipyramidal. Single crystals were obtained by slowly cooling to 5° a 95% alcohol solution saturated at 25°. The crystals showed characteristic elongation and were plastic, as also were crystals of the other orthorhombic modification.[14] Weissenberg and rotating crystal photographs were made with CuK radiation and some rotating crystal photographs were made with MoK α radiations. These data are in part listed in Tables VII and VIII.

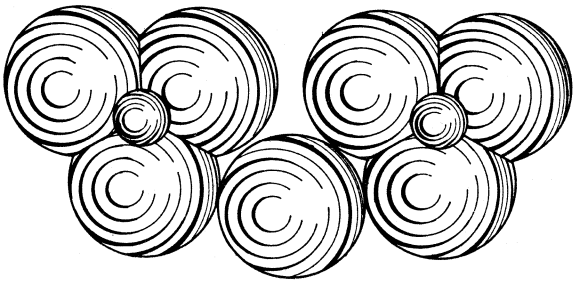


Fig. 5.—A structural element along the c axis in orthorhombic ammonium nitrate (III), stable between 32.3 and 84.2°, along the a axis in the room temperature modification (IV) (−18 to 32°, orthorhombic), and possibly along the a (?) axis of the form (V) stable below −18°. In this, and in Fig. 6, the ammonium group is represented as a sphere, the nitrate group as three oxygen spheres around a central nitrogen atom.

The value of b determined from the spacings of high orders of (010) on Weissenberg photographs is

$$b = 5.45 \text{ Å}.$$

The values of a and c were determined approximately from the layer line separation on a rotating crystal photograph around the long direction of the crystal and from Weissenberg data, respectively. These approximate values are $a = 5.74$, $c = 4.96$ Å. The measured and crystallographically determined axial ratios are:

Measured:	$c:b:a = 0.909:1:1.053$
Crystallographic:	$a:b:c = 0.909:1:1.0553$

[14] Compare W. L. Bond, *Phil. Mag.*, [6] **41**, 1 (1921).

Assuming that b is most accurately measured and that the crystallographic axial ratios are correct, the dimensions of the unit of structure are:

$$a = 5.75 \text{ Å.} \qquad b = 5.45 \text{ Å.} \qquad c = 4.96 \text{ Å.}$$

The density calculated on the basis of such a unit of structure containing $2NH_4NO_3$ is 1.70 g./cc. in agreement with the observed value, 1.72.

If it is assumed that the crystallographically assigned symmetry is correct and that nitrate groups similar to those found in other compounds must be preserved, then all space groups save *Pmma* and *Pmmn* are eliminated. The observed presence of reflections from (001), (110), (103) and (012) cannot be accounted for by *Pmma*. A satisfactory structure can be derived from $Pmmn(V_h^{13})$. The possible atomic positions are

N of NO_3	(a)	$00u;\ \frac{1}{2}\frac{1}{2}\bar{u}$
O of NO_3	(a)	$00w;\ \frac{1}{2}\frac{1}{2}\bar{w}$
N of NH_4	(b)	$0\frac{1}{2}v;\ \frac{1}{2}0\bar{v}$
O of NO_3	(e)	$0\bar{x}y;\ 0xy;\ \frac{1}{2},\frac{1}{2}-x,\bar{y};\ \frac{1}{2},\frac{1}{2}+x,\bar{y}$
or	(f)	$x0y;\ \bar{x}0y;\ \frac{1}{2}-x,\frac{1}{2},\bar{y};\ \frac{1}{2}+x,\frac{1}{2},\bar{y}$

An atomic arrangement with oxygen atoms at (e) is eliminated by the normal decline in the intensities of reflection from $(0k0)$ $(0k_{\text{even}}l)$ and $(0k_{\text{odd}}l)$. There are five parameters to be determined, four in the c direction and one in the a direction.

The observation that (420) *ca.* = (220) and (600) *ca.* = (400) requires $x = 0.18$ to 0.20. Its value is taken as 0.19 ± 0.01. If it is assumed that the oxygen atoms of the nitrate groups are at the corners of equilateral triangles with the nitrogen to oxygen distance 1.25 Å., then

$$w = u + 0.25 \qquad y = u - 0.125$$

Two parameters defining the relative positions of the NO_3 and NH_4 groups remain to be determined.

It is assumed that F_{NH_4} for CuK radiation is approximately the same as determined for MoK radiation diffracted from NH_4Cl,[15] that for oxygen the same as F_0 for oxygen in nickel oxide (CuK radiation),[16] and that for $F_{\text{N of NO}_3} = 0.35\ F_0$ independent of $\sin\theta/\lambda$. Allowing wide variations from these assumptions the observations

$$\begin{aligned}(220)\text{ m. w.} &> (311)\text{a} \\ &> (101)\text{a}\end{aligned}$$

and the observed intensities of reflections from $(00l)$ and $(0kl)$ require

$$u = 0.03 \pm 0.01 \qquad v = 0.57 \pm 0.03$$

It is not considered justifiable to attempt a closer restriction of the parameter values. The agreement between observed and calculated intensities of reflections is shown in Tables VII and VIII.

[15] R. W. G. Wyckoff and A. H. Armstrong, *Z. Krist.*, **72**, 319 (1929).

[16] R. W. G. Wyckoff, *Phys. Rev.*, **35**, 583 (1930).

The structure is partially illustrated in Fig. 6. The structural element shown in Fig. 5 is here repeated in the a rather than in the c direction, the corresponding dimension being 5.75 Å. An ammonium ion is approximately equidistant from six oxygen ions of nitrate groups in the

TABLE VII

WEISSENBERG PHOTOGRAPHIC DATA FROM ORTHORHOMBIC AMMONIUM NITRATE (IV) BELOW 32°

(100) Axis of rotation, equatorial zone. CuK α radiation. Room temperature.

	0k0	0k1	0k2	0k3	0k4	0k5	0k6
00l		v. v. s.	w.	a.	a.	a.	w.
01l		m.	v. s.	m.-m. s.	a.	m. w.	v. w.
02l	v. v. s.	s.	w.	a.	a.	a.	w.
03l		m. w.	m. s.	m. w.	a.	w.	
04l	s.	m.	a.	a.	a.		
05l		v. w.	m. w.	a.			
06l	m.	a.	a.				
08l	m.[a]						

[a] Intensity estimated from CuK β line.

Calculated intensities $I = C\dfrac{1+\cos^2 2\theta}{\sin^2\theta}F\bar{F}$

Plane	Calcd. int.	Plane	Calcd. int.
(001)	1200 C	(011)	130 C
(002)	60 C	(012)	2100 C
(003)	5 C	(013)	1300 C
(004)	10 C	(014)	20 C
(005)	40 C	(015)	30 C
(006)	60 C	(016)	10 C

TABLE VIII

ROTATING CRYSTAL PHOTOGRAPHIC DATA FROM ORTHORHOMBIC NITRATE (IV) BELOW 32°

(100) Axis of rotation; MoKα radiation; room temperature, about 29°.

	Equatorial zone		1st layer line		
Plane	Obs. int.	Calcd. int.	Plane	Obs. int.	Calcd. int.
(010)	a.	0	(110)	s.	2100
(001)	v. s.	1200	(101)	a.	140
(011)	v. w.-a.	130	(111)	v. s.	4500
(020)	v. v. s.	10000	(120)	a.	0
(002)	v. w.	60	(102)	a.	1
(021)	w.	400	(121)	a.	12
(012)	v. s.	2100	(112)	w.	400
(022)	a.	40	(122)	w.	9
(030)	a.	0	(130)		500
(031)	a.	10	(131)	m. w.	550
(003)	a.	5	(103)	m. w.	860
(013)	m.	1300	(113)	a.	40
(032)	m.	1300	(132)	a.	30
(023)	a.	5	(123)	m. w.	1000
(040)	m.	1000	(140)	a.	0

TABLE VIII (*Concluded*)

2d layer line			3d layer line			4th layer line		
Plane	Obs. int.	Calcd. int.	Plane	Obs. int.	Calcd. int.	Plane	Obs. int.	Calcd. int.
(210)	a.	0	(310)	m.	240	(410)	a.	0
(201)	m. s.	1100	(301)	a.	500	(401)	a.	10
(211)	v. s.	4000	(311)	a.	60	(411)	m. w.	260
(220)	m. w.	770	(320)	a.	0	(420)	m. w.	700
(202)	a.	50	(302)	m. s.	500	(402)	a.	2
(221)	m.	1100	(321)		600	(421)	a.	10
(212)	a.	100	(312)	a.	360	(412)	a.	90
(222)	a.	60	(322)	m. w.	540			
(230)	a.	0	(330)		6			
(231)	m.	800	(331)	a.	40			
(203)	w.	160	(303)	a.	1			
(213)	a.	270	(313)	m. w.	150			

plane of the nitrate groups and from six other oxygen ions at a slightly greater distance, three each in planes $\frac{1}{2}b$ above and below it. The distances for the parameter values listed above are: 2.96, 2.96, 2.93, 2.93, 3.14, 3.14, 3.07, 3.07, 3.33, 3.33, 3.33, 3.33 Å. The structure indicates weaker binding normal to the planes of the nitrate groups than in the planes. The slippage accounting for the plasticity of the crystals is, as would be expected, parallel to the plane of the nitrate groups.

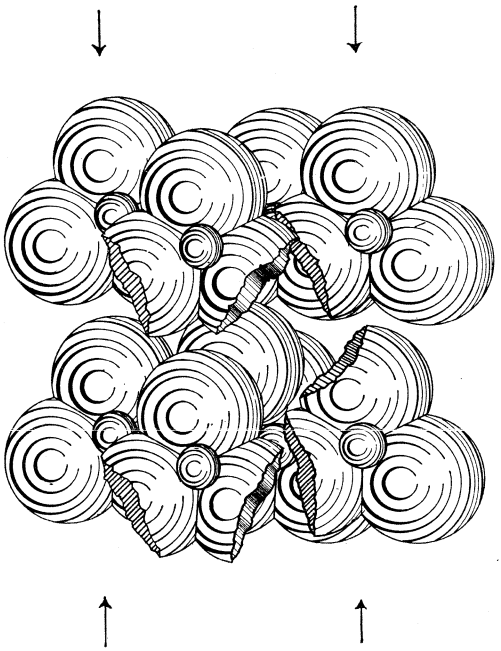


Fig. 6.—Orthorhombic ammonium nitrate (IV) stable between −18 and 32.3°, showing the nitrate groups surrounding an ammonium group.

The Modification Stable below −18° (Hexagonal? V).—Wallerant observed this modification to be uniaxial positive and suggested that the symmetry was tetragonal. Crenshaw and Ritter have recently[17] measured the heat capacities from −90 to 0°. They observed a pronounced maximum in the neighborhood of −60°, the transition being similar in character to that exhibited by certain other ammonium salts. Transitions of this type were interpreted by Pauling as accompanying initiation of molecular rotation. In the case of ammonium chloride x-ray powder diffraction photographs of

[17] Crenshaw and Ritter, *Z. physik. Chem.*, **B16**, 143 (1932).

samples below and above the transition region showed no essential changes other than those due to expansion of the lattice.[18] As we have previously pointed out, these results are not inconsistent with the concept of molecular rotation.[2]

The transition V $\rightleftharpoons$ IV (−18°) was not recorded by Crenshaw and Ritter. There is, however, no possible ambiguity about the existence of this phase transformation. We have observed it under the microscope, by thermal analysis, and with a dilatometer. The x-ray powder diffraction patterns give final evidence of a change in phase. Although this transition is sluggish, and often is delayed so that it occurs on heating in the neighborhood of −5°, it nevertheless seems as if it should have been observed in the heat capacity measurements.

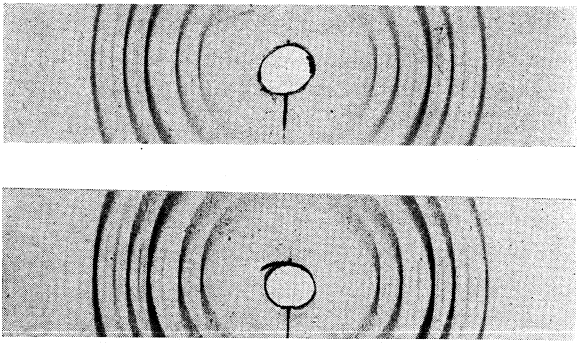


Fig. 7.—(a) A powder diffraction pattern of hexagonal ammonium nitrate (V) at −33°. CuK α radiation. (b) Same as (a), at −78°.

We have made x-ray powder diffraction photographs with CuK radiation of samples of ammonium nitrate at −33° (liquid ammonia) and −78° (solid carbon dioxide). Two such photographs are reproduced as Fig. 7. The photographs, with the exception of a displacement of the pattern due to thermal expansion, are the same within the limits of observation (fine lines will probably not show in the reproduced photographs). The ammonium group is probably rotating at −33°, and in the four modifications stable at higher temperatures and atmospheric pressure. This comment is speculative in that x-ray diffraction characteristics are not sufficient to afford an answer to the question.

Data obtained from photographs of ammonium nitrate at −78° are listed in Table IX. There apparently is one diffraction maximum very close to the central image; however, it was not definitely proved that this actually is a part of the diffraction pattern. The positions of the maxima, including the innermost, are given by

[18] Simon and Simson, *Naturwissenschaften*, **38**, 880 (1926).

$$\sin^2\Theta = 0.0242\,(h^2 + hk + k^2) + 0.00234\,l^2$$

for CuK α_1 radiation. This corresponds to a hexagonal lattice having $a = 5.72$, $c = 15.9$ Å. The density calculated on the basis of a unit of structure containing $6NH_4NO_3$ is 1.76 g./cc. in agreement with 1.74, the determined value. It is to be emphasized that this integral number, 6, of NH_4NO_3, in the unit of structure would be most unusual if the lattice dimensions were obtained from a spurious agreement between observed and calculated $\sin^2\Theta$ values.

TABLE IX

POWDER PHOTOGRAPHIC DATA FROM HEXAGONAL (?) AMMONIUM NITRATE (V) BELOW $-16°$

CuK α radiation; temperature, $-78°$; $\sin^2\Theta = 0.0242\,(h^2 + hk + k^2) + 0.00234\,l^2$.

Plane	$\sin^2\Theta$ (calcd.)	$\sin^2\Theta$ (obs.)	Est. intensity	Plane	$\sin^2\Theta$ (calcd.)	$\sin^2\Theta$ (obs.)	Est. intensity
(001)	0.00234	0.0018	w.	(113)	0.0937	0.0912	0.5
(002)	.00936			(200)	.0968	.0984	2.0
(003)	.0211			(201)	.0991		
(100)	.0242	.0245	5.0	(202)	.1062		
(101)	.0265			(106)	.1085	.1086	2.0
(102)	.0335			(114)	.1100		
(004)	.0375	.0375	6.0	(007)	.1136		
(103)	.0453			(203)	.1178	.1174	8.0
(005)	.0585			(115)	.1311		
(104)	.0616	.0621	10.0	(204)	.1342	.1356	0.5
(110)	.0726	.0725	1.0	(107)	.1378		
(111)	.0749	.0744	0.5	(008)	.1497	.1463	0.5
(112)	.0819	.0804	0.5	(205)	.1553	.1550	0.5
(105)	.0827	.0832	8.0				
(006)	.0842						

The value of a_0 (5.72 Å.) is approximately the same as a_0 (5.75 Å.) of the room temperature modification, c_0 (5.80 Å.) of the second orthorhombic modification, and a_0 (5.74 Å.) of the tetragonal form. It is possible that it coincides with the direction of characteristic elongation, as is the case for the two orthorhombic modifications. This, the positive optical character, and the value of maximum index of refraction, clearly show that the planes of the nitrate groups are approximately parallel to the c axis. The intensities of reflections from the various orders of (001) are most unusual; (001) w. or a., (002)a., (003)a., (004)m. s., (005)a., (007)a., (008)w. w. We were unable to see the manner in which such an intensity distribution could be obtained in a hexagonal lattice with the atomic arrangement restricted as mentioned above. The, at least, pseudo-uniaxial character and hexagonal lattice require the nitrate groups to be approximately repeated in one or two groups of three planes containing the optic axis at angles of 20°. If in such a case the nitrate groups were not distributed according to hexagonal symmetry along the c axis, the crystals would

nevertheless be approximately uniaxial. For these reasons we would consider it quite possible that the symmetry may be orthorhombic, monoclinic or triclinic.

Summary

The structures of three of the six crystalline modifications of ammonium nitrate have been determined and data, leading to partial structure determinations, have been obtained from two other forms. The nitrate groups are rotating in at least three orthogonal directions in the cubic (I) form which is stable between 125.2 and 169.5°; $a_0 = 4.40$ Å., $1NH_4NO_3$ in the unit of structure. The structural characteristics of the other modifications examined are:

Tetragonal (II) (125.2 − 84.2°) $a = b = 5.75$ Å., $c = 5.00$ Å., $2NH_4NO_3$ in the unit of structure. $2NH_4$ at 00; $\frac{1}{2}\frac{1}{2}$; 2N of NO_3 at $0\frac{1}{2}$, $\frac{1}{2}0$; 2 oxygen at $0\frac{1}{2}$, $\frac{1}{2}0$; 4 oxygen at xy, $\bar{x}\bar{y}$, $\bar{y}x$, $y\bar{x}$, with $x = 0.14$, $y = 0.36$. The arrangement in the c direction was not determined.

Orthorhombic (III) (84.2 − 32.3°) $a = 7.06$ Å., $b = 7.66$ Å., $c = 5.80$ Å., $4NH_4NO_3$ in the unit of structure. Space group $Pbnm(V_h^{16})$, 8 oxygens in general positions with $x = -0.07$, $y = -0.27$, $z = 0.06$, 4 oxygen on reflection planes with $u_1 = -0.19$, $v_1 = -0.05$, $4NH_4$ on reflection planes with $u_2 = 0.30$, $v_2 = 0.52$, 4 nitrogen on reflection planes with $u_3 = -0.09$, $v_3 = -0.19$. The parameter values are probably accurate to ±0.03.

Orthorhombic (IV) (32.3° to −18°) $a = 5.75$ Å., $b = 5.45$ Å., $c = 4.96$ Å., with $2NH_4NO_3$ in the unit of structure. Space group $Pmmn(V_h^{13})$ with 4 oxygen at $x0y$; $\bar{x}0y$; $\frac{1}{2}-x,\frac{1}{2},\bar{y}$; $\frac{1}{2}+x,\frac{1}{2},\bar{y}$, with $x = 0.19$, $y = -0.095$, oxygen and 2 nitrogen at $00u$, $\frac{1}{2}\frac{1}{2}\bar{u}$, with parameter 0.28 and 0.03, respectively, and $2NH_4$ at $0\frac{1}{2}v$; $\frac{1}{2}0\bar{v}$ with $v = 0.57$.

The form (V) stable below −18° gives a powder diffraction pattern in agreement with a hexagonal unit of structure having $a = 5.75$ Å., $c = 15.9$ Å. containing $6NH_4NO_3$. The data indicate that the true lattice might be only pseudo-hexagonal. Diffraction patterns of samples at −33 and −78° are identical save for displacement due to expansion, despite the existence of a gradual transition at *ca.* − 60°.

WASHINGTON, D. C.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 313]

THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDRAZINE

BY RALPH R. WENNER AND ARNOLD O. BECKMAN

RECEIVED APRIL 4, 1932 PUBLISHED JULY 6, 1932

Introduction

The photochemical decomposition of gaseous hydrazine by the total radiation from a quartz mercury arc and the photosensitized decomposition by excited mercury atoms have been studied by Elgin and Taylor.[1] The products of the decomposition were identified as ammonia, hydrogen and nitrogen. A minimum quantum yield of thirteen molecules of hydrazine decomposed per quantum absorbed was obtained for the photosensitized decomposition by comparing the rate of decomposition of the hydrazine with the rate of formation of water from hydrogen and oxygen under similar conditions. No determination was made of the quantum yield for the purely photochemical decomposition.

The present investigation is concerned with the determination of the quantum yields in the photochemical decomposition of gaseous hydrazine by monochromatic radiation of wave length 1990 Å.

Experimental Method

Preparation of Anhydrous Hydrazine.—The anhydrous hydrazine was prepared by the dehydration of hydrazine hydrate with fused potassium hydroxide. Hydrazine hydrate, obtained from the Eastman Kodak Company, was refluxed for three hours in an atmosphere of hydrogen with fused potassium hydroxide in an all-Pyrex glass apparatus. The hydrazine was then distilled in a stream of hydrogen at a pressure of 30 to 100 millimeters of mercury. The distillate was refluxed with more potassium hydroxide and again distilled. This process was repeated three times. Analysis of the distillate by the iodate method[2] indicated a purity of 98.9%.

Barium monoxide is recommended by Hale and Shetterly[3] for the dehydration of hydrazine hydrate. It was found in the present work that even the best available barium monoxide was less satisfactory than the fused potassium hydroxide which was used.

The product from the above operations was given a final distillation from potassium hydroxide in a stream of nitrogen. Three fractions were collected and sealed off in tubes containing fused potassium hydroxide. Each tube contained an internal thin-walled tip which could be broken by means of a glass-encased magnetically operated hammer after the tube had been sealed to the vacuum system and the system evacuated. The middle fraction of the anhydrous hydrazine was introduced into the system in this manner without exposure to the atmosphere after the final distillation. The hydrazine was distilled *in vacuo* at room temperature into a series of smaller similar tubes (containing fused potassium hydroxide) which were stored in the dark and attached to the vacuum system as needed.

[1] Elgin and Taylor, THIS JOURNAL, **51**, 2059 (1929).

[2] Bray and Cuy, *ibid.*, **46**, 1858 (1924).

[3] Hale and Shetterly, *ibid.*, **33**, 1071 (1911).

Apparatus.—A diagram of the apparatus is shown in Fig. 1. Anhydrous liquid hydrazine (prepared as described above) was stored in contact with fused potassium hydroxide in the reservoir B, which was attached to the vacuum system. The vacuum system consisted essentially of a fused quartz reaction cell L in which the hydrazine was irradiated, a McLeod gage (attached at E) for reading the total pressure of nitrogen and hydrogen produced by the decomposition, a quartz fiber gage H for analyzing the nitrogen–hydrogen mixture, and several mercury cut-offs and freezing-out traps. The system was evacuated by a mercury vapor pump through the cut-off A. The quartz fiber gage H consisted of a single fiber of elliptical cross section and was fitted with an electromagnetic starting device.[4] Some trouble was experienced initially from room vibrations but this difficulty was eliminated by mounting the gage on a very massive support which rested upon several layers of hair felt. The use of the quartz fiber gage as a means for analyzing nitrogen–hydrogen mixtures has been shown to give satisfactory results.[5]

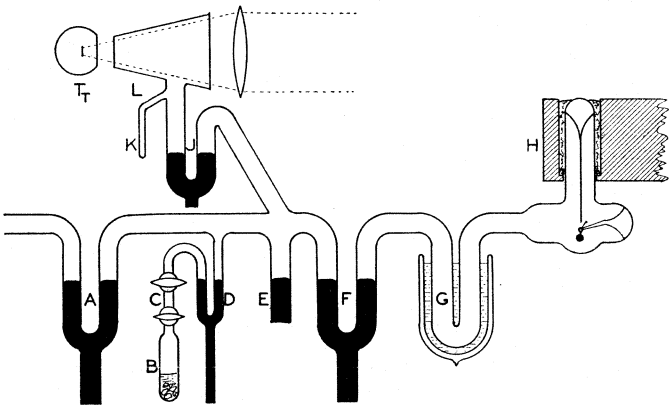


Fig. 1.—Diagram of apparatus.

Monochromatic radiation of wave length 1990 Å. was obtained by the use of a condensed aluminum spark and a Bausch and Lomb ultraviolet monochromator in the manner previously described.[6] The beam of monochromatic light emerging from the monochromator passed through two converging cylindrical quartz lenses, through the plane fused quartz windows of the reaction cell L and onto the receiving vane of a sensitive vacuum thermopile T_t (transmission thermopile). The reaction cell was constructed with the front window at an angle of 45° with the axis of the cell so that a fraction of the incident radiation was reflected at right angles onto the receiving vane of a similar thermopile T_r (reflection thermopile). The thermopiles were connected to two Leeds and Northrup high-sensitivity galvanometers which were set up in conjunction with an automatic recording device so that continuous records were made of the deflections of both galvanometers. From these continuous records the amount of radiant energy absorbed by the reaction mixture could be determined for each run with an accuracy which was independent of fluctuations in the intensity of the radiation or of changes in the absorption of the mixture during the run.

The vanes of the thermopiles were large enough to cover completely the converged beams. The thermoelectric system of each thermopile consisted of six junctions

[4] Beckman, *J. Opt. Soc.*, **16**, 276 (1928).

[5] Beckman and Dickinson, THIS JOURNAL, **50**, 1870 (1928).

[6] Beckman and Dickinson, *ibid.*, **52**, 124 (1930).

of bismuth and bismuth-tin alloy (95% Bi, 5% Sn) in series, three junctions attached to each vane. The thermopiles were mounted in glass containers with plane fused quartz windows attached with wax. The thermopile vessels were continuously evacuated during the runs so that constant sensitivity was secured. Liquid-air traps prevented the access of mercury vapor into the thermopile vessels.

The continuous recording device consisted of a flat carriage which carried a 25 × 31 cm. sheet of photograph paper and was moved vertically at a constant speed by means of a screw which was driven by a synchronous motor. Two beams of light from a strongly illuminated vertical slit were reflected from the two galvanometer mirrors and focused upon the photographic paper by means of two one-diopter spherical lenses placed directly in front of the galvanometer mirrors. A 50-diopter cylindrical lens which extended horizontally across the width of the paper changed the narrow lines of light thus formed into two intense circular spots of light less than half a millimeter in diameter. The apparatus was adjusted so that the zero positions of the two spots of light were near the two edges of the paper with the deflections toward the opposite edges. This arrangement permitted the utilization of the full width of the paper for each beam, as no confusion resulted from the crossing of the two beams. To avoid the error caused by shrinkage on expansion of the paper during development, drying, etc., the coördinate system was printed upon the paper immediately after removal from the recorder by making a contact print through a coördinate screen made by ruling fine transparent coördinate lines through an opaque silver coating on a glass plate.

The thermopiles, galvanometers and leads were carefully shielded, thereby obtaining complete freedom from electrical disturbances caused by the spark. The galvanometer deflections were found to be exactly proportional to the galvanometer current throughout the range used in these experiments. The thermopiles were of the compensated type, to avoid difficulties occasioned by shifting zero positions. It was found that the zero positions were quite constant and the error introduced from this source was negligible.

Calibration.—The determination of the number of quanta absorbed by the reaction mixtures required the following data: (1) the calibration of the transmission thermopile T_t, (2) the transmission factors for λ1990 Å. of the rear window of the reaction cell and the window of the thermopile T_t, and (3) the ratio of the galvanometer deflections for thermopiles T_r and T_t with the cell evacuated. To calibrate thermopile T_t carbon lamps calibrated by the Bureau of Standards were used. A brass plate with a hole of known area was placed in front of the thermopile window in such a way that light from the standard lamp passing through the hole was entirely intercepted by the receiving vane. The intensity of radiation at the hole was known from the calibration of the standard lamp. The transmission of the thermopile window for this radiation had been determined by previous experiments to be 0.914. By dividing the product of the intensity of radiation, the area of the hole and the transmission of the window by the scale deflection, the number of ergs per second required for unit deflection was obtained. A number of determinations at various lamp currents using two standard lamps gave consistent results with the average value 1.230 ergs per second per unit of deflection.

The transmissions for λ1990 Å. of the rear window of the cell and the window of thermopile T_t were obtained before the cell was assembled, with the aid of the continuous recording device. With both thermopiles in place, a piece of thin quartz plate was placed in the position later taken by the front window of the cell and a record of the galvanometer deflections was taken with the spark in operation. The rear window of the cell was then placed in front of thermopile T_t in the position it would ultimately occupy when the cell was in place, and another record of the galvanometer deflections taken. The transmission of the window was then found from a comparison of the two records. Five such determinations gave a mean value of 0.720 for the transmission of the rear

cell window. For convenience, to prevent dismantling thermopile T_t, a duplicate window from the same stock of quartz was substituted for the actual thermopile window in determining the transmission of the latter. The mean value of five determinations of the transmission of the thermopile window was 0.653.

The ratio of the galvanometer deflections for the two thermopiles with the cell evacuated was checked several times during the course of the investigation. For runs 1 to 9 the ratio was 3.15 and for runs 10 to 22 the ratio was 2.86, the different values being due to a change in the apparatus between runs 9 and 10.

Procedure.—The procedure was as follows in a typical quantum yield determination. With the system evacuated, cut-offs A and F closed, cut-offs D and J opened, and with the mercury in the McLeod gage connection E as high as possible, the desired amount of hydrazine was admitted through the doser C. Cut-off D was then closed and a mixture of ether and solid carbon dioxide was applied to the trap K to freeze the hydrazine. The system was then evacuated to remove any traces of non-condensable gas which might be present. Cut-off J was then closed and the freezing mixture removed from the trap K, allowing the hydrazine to vaporize. The freezing mixture was again applied, cut-off J opened and the system again evacuated. This process was repeated a third time. With cut-off J closed and the freezing mixture removed, the pressure of the hydrazine was measured by the difference in mercury levels in the cut-off J. A sheet of photographic paper was put into the recorder and the galvanometer switches were closed. The hydrazine was then irradiated for a definite time, usually fifteen minutes, after which liquid air was applied to the trap K, cut-offs A and D were closed, cut-off F was opened and the connection made with the McLeod gage. (Liquid air was kept on the trap G throughout the run to keep mercury vapor out of the quartz fiber gage H.) Cut-off J was then opened allowing the non-condensable gases to flow into the McLeod and quartz-fiber gages on which readings were taken. The coördinate system was printed upon the photographic paper and the paper was developed.

It was found that when gaseous hydrazine stood in the reaction cell there was a slow development of non-condensable gas even in the dark, presumably due to some slow wall reaction, since the rate of pressure development was greatest when the cell was new or freshly cleaned and decreased after the cell had been in use for some time. To correct for this effect, the system was evacuated after the above readings were taken, cut-off J closed, the liquid air removed from the trap K and the hydrazine allowed to stand in the reaction cell for the same length of time as during the run. Liquid air was then applied at K, cut-off J opened and the pressure of the non-condensable gas read on the McLeod gage, all mercury levels being at the same levels as before. This pressure correction was always small, amounting to only 1 or 2% of the total pressure of non-condensable gas. The pressures were so small that satisfactory quartz

fiber readings for a composition correction could not be made. However, experiments extended over longer time intervals indicated that the non-condensable gas produced in the dark was of nearly the same composition as the non-condensable gas produced photochemically, so no appreciable error was introduced by neglecting entirely any slight changes in composition which might have been produced by the very small amounts of products of the dark reaction.

Experimental Results

The products of the decomposition have been identified by Elgin and Taylor as ammonia, hydrogen and nitrogen. The presence of ammonia was confirmed in the present investigation by the Nessler test. This test was made after irradiation by freezing the undecomposed hydrazine with ether–carbon dioxide mixture. The ammonia was then frozen in a side tube by applying liquid air. This tube was sealed off from the apparatus and the tip broken under ammonia-free water. Upon adding Nessler's reagent to the solution, a distinct reddish brown color developed proving the presence of ammonia. Blank tests without irradiation proved the absence of ammonia in the hydrazine.

The results of the quantum yield determinations are given in Tables I and II in which the runs are arranged for convenience in order of decreasing hydrazine pressure. In Table I are given the data from which may be calculated the number of molecules of hydrazine decomposed during each run. In the second column is given the initial pressure of hydrazine in the cell, which is also the pressure throughout the entire run since in none of the runs was more than 0.1% of the hydrazine decomposed. The temperature of the system is given in the third column and the total pressure of the non-condensable products in the fourth column. From the latter value must be subtracted the correction pressure for the dark reaction, given in the next column, to obtain the true pressure of the hydrogen plus nitrogen produced by the photochemical decomposition. In the sixth column is given the value for X_{H_2}, the mole fraction of hydrogen in the non-condensable gas as determined by the quartz fiber gage. In the last column is given the number of molecules of hydrazine decomposed, calculated from the equation

$$N_{N_2H_4} = \frac{4\,\overline{N}\,P_{H_2+N_2}\,V}{760\,RT}\,(3/4 - X_{H_2}) \qquad (1)$$

where $\overline{N}$ is the Avogadro number and R has the value of 82.1 cc. atm. per degree. V is the effective volume of the system determined experimentally by air expansion with liquid air on traps G and K exactly as in the measurement of the non-condensable gas pressures. For runs 1 to 9 the volume was 137.2 cc. and for runs 10 to 22 the volume was 141.9 cc. The above equation may be obtained from the perfect gas law and the consideration

that the number of gram atoms of hydrogen and nitrogen in the products (NH_3, H_2 and N_2) must equal the number of gram atoms of hydrogen and nitrogen in the decomposed N_2H_4.

In Table II are given the data from which may be calculated the number of quanta of radiation absorbed during each run. The duration of the irradiation in seconds is given in column 2. In columns 3 and 4 are given the mean values D_t and D_r of the galvanometer deflections for the transmitted (thermopile T_t) and the reflected (thermopile T_r) beams, obtained from the continuous photographic record. In column 5 is given the total number of quanta of radiation of wave length 1990 Å. which entered the reaction mixture during the run, computed from the relation

$$Q_E = \frac{1.230\ \beta\ D_r\ t}{\alpha_1\alpha_2\ hc/\lambda} = 2.65 \times 10^{11}\ \beta\ D_r\ t \qquad (2)$$

the factor 1.230 being the number of ergs per second of radiation falling on the vane of thermopile T_t for unit deflection. β is the ratio of the galvanometer deflections for thermopile T_r to the deflections for thermopile T_t with the reaction cell evacuated, and t is the time of irradiation. α_1 and α_2 are the transmission factors of the rear cell window and the window of thermopile T_t for radiation λ 1990 Å. and have the values 0.720 and

TABLE I

DATA FOR CALCULATING AMOUNT OF HYDRAZINE DECOMPOSED

1 Run	2 Press. N_2H_4, mm.	3 Temp., °A.	4 Press. non-cond., mm. × 10^3	5 Press. corr., mm. × 10^3	6 X_{H_2}	7 Molecules N_2H_4 decomp. × 10^{-16}
22	14.0	298	3.06	0.05	0.587	9.05
1	13.0	300	4.15	.06	.582	12.22
2	13.0	301	3.83	.05	.582	11.27
17	12.0	298	2.97	.05	.613	7.41
18	12.0	298	3.00	.05	.611	7.57
5	11.0	299	3.99	.05	.598	10.72
10	10.5	302	3.11	.08	.628	6.75
6	10.0	298	3.64	.05	.608	9.13
13	9.8	300	2.99	.07	.616	7.19
3	8.0	300	4.06	.05	.618	9.39
4	8.0	301	3.91	.07	.621	8.78
15	7.0	300	3.22	.06	.629	7.05
16	7.0	298	3.07	.08	.619	7.21
9	6.0	299	3.63	.06	.613	8.73
11	6.0	302	3.04	.08	.644	5.75
19	5.0	298	2.81	.06	.639	5.62
20	5.0	298	2.91	.06	.634	6.10
21	3.5	300	2.68	.05	.634	5.61
8	3.0	300	3.47	.06	.622	7.76
12	3.0	302	2.59	.08	.644	4.85
14	2.0	298	2.33	.08	.629	5.03
7	2.0	299	2.85	.06	.634	5.77

TABLE II

DATA FOR CALCULATING AMOUNT OF RADIATION ABSORBED

1 Run	2 Expt. time, sec.	3 Galv. defl., D_r	4 Galv. defl., D_t	5 Quanta entering $\times 10^{-15}$	6 Quanta leaving $\times 10^{-15}$	7 Quanta absorbed $\times 10^{-15}$	8 Quantum yield, Y
22	780	9.38	0.00	5.55	0.00	5.55	1.63
1	900	9.58	.56	7.22	.13	7.09	1.72
2	900	9.48	.93	7.16	.22	6.94	1.63
17	780	9.31	.00	5.52	.00	5.52	1.34
18	780	9.64	.00	5.72	.00	5.72	1.33
5	870	11.49	.89	8.37	.20	8.17	1.31
10	780	8.54	.39	5.05	.08	4.97	1.35
6	900	9.37	1.12	7.06	.27	6.79	1.34
13	787	9.58	0.74	5.73	.15	5.58	1.29
3	900	11.40	1.68	8.58	.40	8.18	1.14
4	900	9.87	1.13	7.43	.27	7.16	1.23
15	780	11.13	1.55	6.58	.32	6.26	1.12
16	780	10.42	1.46	6.16	.30	5.86	1.23
9	900	11.07	1.67	8.34	.39	7.95	1.10
11	780	10.82	1.74	6.40	.36	6.04	0.96
19	780	10.22	1.90	6.05	.39	5.66	1.00
20	780	9.81	2.24	5.81	.46	5.35	1.14
21	780	9.93	4.55	5.88	.94	4.94	1.13
8	900	10.83	4.26	8.15	1.02	7.13	1.09
12	780	9.17	5.57	5.42	1.15	4.27	1.13
14	780	10.03	9.95	5.93	2.06	3.87	1.30
7	900	10.92	8.99	8.22	2.14	6.08	0.96

0.653, respectively. In column 6 is given the total number of quanta which left the reaction mixture, as computed from the relation

$$Q_L = \frac{1.230\, D_t\, t}{\alpha_1 \alpha_2\, hc/\lambda} = 2.65 \times 10^{11}\, D_t\, t \qquad (3)$$

By subtracting the value in column 6 from that in column 5 there is obtained the value given in column 7, namely, the total number of quanta absorbed by the reaction mixture during the run. Finally by dividing the value in column 7, Table I, by the corresponding value in column 7, Table II, the photochemical yield, Y, recorded in column 8, is obtained. This value represents the number of molecules of hydrazine decomposed per quantum absorbed of radiation of wave length 1990 Å.

Before discussing the relation between quantum yield and the pressure of hydrazine, attention should be called to the fact that the calculated values of Y are greatly affected by small errors in the determination of X_{H_2}, as will be seen from Equation 1. Thus, with a value $X_{H_2} = 0.60$, an error of 0.01 in X_{H_2} will cause an error of about 7% in the value of Y. To avoid the use of this equation, attempts were made to measure the ammonia pressures directly, as was done at higher pressures by Elgin and Taylor by freezing the hydrazine with ether–carbon dioxide mixture. It was found, however, that it was impossible to measure ammonia pressure

accurately at very low pressures. Since the values of X_{H_2} are known with considerable accuracy, it was felt that the direct measurement of the ammonia pressure would introduce greater errors than are introduced by the use of Equation 1.

It will be seen from column 8, Table II, that despite random variations, there is a definite increase in the quantum yield with increasing pressure of hydrazine, the values of Y ranging from about unity at the lower pressures to a value of 1.7 at the higher pressures. The quantum yield at pressures higher than 14 mm. could not be studied at room temperature since this pressure is the saturation pressure of hydrazine. At pressures lower than 2 mm. the light absorption was so small that neither the amount of radiation absorbed nor the amount of products formed could be measured satisfactorily.

The values of X, the mole fraction of hydrogen in the non-condensable gas, which are recorded in column 6 of Table I, also show a variation with the hydrazine pressure, a mole fraction $X = 0.58$ being obtained at the higher pressures and a mole fraction $X = 0.64$ at the lower pressures.

Discussion

The results of the present investigation are not in agreement with the conclusions of Elgin and Taylor[1] that the photochemical decomposition of hydrazine proceeds according to the stoichiometric relation

$$2\ N_2H_4 = 2\ NH_3 + N_2 + H_2$$

with the subsequent decomposition of the ammonia. If this conclusion is correct, then the mole fraction X of hydrogen in the non-condensable gas must be exactly 0.50 at the start of the decomposition before an appreciable amount of ammonia has decomposed. In the present experiments less than 0.1% of the hydrazine was decomposed in any run and it was found that the mole fraction of hydrogen varied from 0.58 at the higher hydrazine pressures to 0.64 at the lower pressures. These values do not agree with the analyses of the non-condensable gas reported by the previous investigators (Ref. 1, Table I) which showed approximately 50 mole per cent. of hydrogen even when more than one-fourth of the hydrazine was decomposed. The authors state that the analysis was accomplished by burning the hydrogen with copper oxide and that from five to six hours were required for the completion of an analysis, due to the slow diffusion of the gases. Under such conditions it is conceivable that the observed percentage of hydrogen may be too low on account of incomplete combustion. Indeed, it may be mentioned that if X is computed from their recorded values of ammonia and non-condensable gas pressures, using the stoichiometric relation

$$X = {}^2/_3 - \frac{p_{NH_3}}{6\ p_{H_2 + N_2}}$$

a minimum value of $X = 0.57$ is obtained. Therefore, since the initial value of X is not 0.50, but since, as our experiments show, the value of X is a function of the hydrazine pressure, it appears that the photochemical decomposition of hydrazine does not follow the simple stoichiometric equation given above but must proceed in at least two different ways, one of which yields low values of X and is favored at high pressures while the other yields higher values of X and is favored at low pressures.

Elgin and Taylor[1] have discussed at some length possible mechanisms for the decomposition of hydrazine. They found that the results of their investigations of the photosensitized decomposition could be explained by either of the following mechanisms

(a)
$$N_2H_4 + Hg' = N_2H_4' + Hg = N_2H_3 + H + Hg \quad (1)$$
$$N_2H_3 + N_2H_4 = 2\,NH_3 + N_2 + H \quad (2)$$
$$H + N_2H_4 = N_2H_3 + H_2 \quad (3)$$

wall reactions:
$$H + H = H_2 \quad (4)$$
$$N_2H_3 + H = N_2H_4 \quad (5)$$

(b)
$$NH_2 + N_2H_4 = NH_3 + N_2 + H_2 + H \quad (2)$$
$$H + N_2H_4 + NH_2 + NH_3 \quad (3)$$

wall reactions:
$$H + H = H_2 \quad (4)$$
$$NH_2 + NH_2 = N_2H_4 \quad (5)$$

It will be seen that each of these mechanisms will account for a high quantum yield (their observed minimum quantum yield = 13 molecules N_2H_4 decomposed per quantum absorbed) and for the failure of hydrogen to retard the rate of the decomposition. The failure of hydrogen to retard the rate of decomposition was observed for both the photochemical and photosensitized decompositions but is of particular interest only for the latter case where hydrogen atoms are known to be formed by collisions between excited mercury atoms and hydrogen molecules. Although the above mechanisms were formulated on the basis of the results of their investigation of the photosensitized decomposition, the authors state "there is no reason to believe that the purely photochemical decomposition proceeds by another mechanism." It is clear, however, that the new experimental data disclosed in the present article show that the purely photochemical decomposition cannot be explained by either of the above mechanisms for the following reasons. (1) The low quantum yield for the photochemical decomposition does not indicate a chain mechanism. (2) The observed mole fraction of hydrogen in the products is greater than given by the above mechanisms.

In the photochemical decomposition of gaseous hydrazine produced by the absorption of radiation of wave length 1990 Å. the primary step undoubtedly involves the splitting of the molecules into substituent parts,

since this radiation lies well within the region of continuous absorption.[1,7] Whether the splitting occurs at a N–H bond or at the N–N bond has not yet been established. Although Imanishi has concluded that the absorption of 5.5 volt radiation (2244 Å.) causes a rupture of the N–N bond, his conclusions are merely conjectures and are without experimental support. If one assumes that the primary dissociation results in the splitting of a hydrogen atom from the hydrazine molecule, a mechanism can be readily set up which will account for the experimental facts.

The steps in the mechanism are as follows

$$N_2H_4 + h\nu = N_2H_3 + H \quad (1)$$
$$H + N_2H_4 = N_2H_3 + H_2 \quad (2)$$
$$2N_2H_3 = 2NH_3 + N_2 \quad (3)$$
$$2N_2H_3 = N_2 + H_2 + N_2H_4 \text{ (wall reaction)} \quad (4)$$

This mechanism assumes that collisions between N_2H_3 and N_2H_4 molecules do not result in chemical reaction. The N_2H_3 molecules can react with themselves in two competing reactions, namely, a homogeneous bimolecular reaction resulting in the formation of ammonia and a wall reaction resulting in the regeneration of hydrazine.

It may be seen that this mechanism is in substantial agreement with the experimental data. The quantum yield lies within the range one to two. The mole fraction of hydrogen in the non-condensable gases lies between the limits one-half and two-thirds. Further, the quantum yield increases and the mole fraction of hydrogen decreases with increasing hydrazine pressure, since increasing pressure favors reaction 3 in comparison with reaction 4.

Upon the basis of the above mechanism a definite relationship should exist between the quantum yield Y and the mole fraction of hydrogen X; namely

$$Y = \frac{4X - 3}{X - 1}$$

A comparison of the observed quantum yields with the quantum yields calculated from this equation using the observed mole-fractions of hydrogen is given in Table III. The fact that the calculated values are slightly higher than the observed values except at the higher pressures suggests the possible occurrence of other wall reactions such as

$$H + N_2H_3 = N_2H_4 \quad (5)$$
$$H + H = H_2 \quad (6)$$

which would have the effect of lowering the quantum yields with decreasing pressure.

On the basis of the above mechanism, it is evident that the value of Y depends upon the manner in which the N_2H_3 molecules divide themselves between the homogeneous and heterogeneous reactions. If α represents

[7] Imanishi, *Nature*, **127**, 782 (1931).

TABLE III

COMPARISON OF OBSERVED AND CALCULATED QUANTUM YIELDS

Press. N_2H_4 mm.	X_{H_2}	$Y_{obs.}$	$Y_{calcd.}$	Press. N_2H_4, mm.	X_{H_2}	$Y_{obs.}$	$Y_{calcd.}$
14.0	0.587	1.63	1.58	7.0	0.629	1.12	1.29
13.0	.582	1.72	1.60	7.0	.619	1.23	1.37
13.0	.582	1.63	1.60	6.0	.613	1.10	1.42
12.0	.613	1.34	1.42	6.0	.644	0.96	1.18
12.0	.611	1.33	1.44	5.0	.639	1.00	1.22
11.0	.598	1.31	1.52	5.0	.634	1.14	1.26
10.5	.628	1.35	1.32	3.5	.634	1.13	1.26
10.0	.608	1.34	1.45	3.0	.622	1.09	1.35
9.8	.616	1.29	1.41	3.0	.644	1.13	1.18
8.0	.618	1.14	1.39	2.0	.629	(1.30)	1.29
8.0	.621	1.23	1.37	2.0	.634	0.96	1.26

the fraction of N_2H_3 molecules which react on the walls according to Equation 4, then $\alpha = 2 - Y$. From the observed values of Y it follows that from 0 to 70% the N_2H_3 molecules react homogeneously to form ammonia and 100 to 30% react upon the wall with the partial regeneration of hydrazine.

Summary

The quantum yields for the photochemical decomposition of gaseous hydrazine by monochromatic radiation of wave length 1990 Å. have been investigated over the pressure range 2 to 14 millimeters of mercury. It was found that the quantum yields range from 1.0 (molecules of N_2H_4 decomposed per quantum of radiation absorbed) at the lower pressure to 1.7 at the higher pressure.

The products of the decomposition were found to be ammonia, nitrogen and hydrogen, in agreement with the results of previous investigators, but the relative proportions of these substances are in disagreement with the earlier data. It was found that the composition of the products is a function of the hydrazine pressure, with more hydrogen formed at the low hydrazine pressures than at the high pressures.

It is shown that the mechanisms which have been previously proposed for the photosensitized decomposition of hydrazine are not applicable to the photochemical decomposition. A possible mechanism for the latter is suggested which is consistent with the experimental data.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY]

VAPOR PRESSURES, EVAPORATION, CONDENSATION AND ADSORPTION

BY IRVING LANGMUIR

RECEIVED APRIL 6, 1932 PUBLISHED JULY 6, 1932

The adsorption of gases or vapors on solids is due to the time lag between the condensation and the evaporation of the molecules from the surface. The relation between the pressure and the amount of gas adsorbed thus depends primarily upon the laws of condensation and of evaporation. In an earlier paper[1] several different relationships for condensation and evaporation were chosen to illustrate some simple typical examples of adsorption phenomena.

In Case I, which was there considered as "simple adsorption," it was postulated that the forces acting between adjacent adsorbed atoms or molecules[2] are negligible, so that the average life of each adsorbed atom (adatom) is independent of the presence of others on the surface. If θ represents the fraction of the surface covered by adatoms, the rate of evaporation ν is thus equal to $\nu_1\theta$, where ν_1 is the rate of evaporation from a completely covered surface. It was also assumed, for the sake of simplicity, that atoms condense only on that part of the surface which is bare, so that the rate of condensation was taken to be $\alpha_0\mu(1 - \theta)$, where μ, the rate at which incident atoms strike the surface per unit area is given by

$$\mu = (2\pi mkT)^{-1/2} p = 2.653 \times 10^{19} p(MT)^{-1/2} \qquad (1)$$

p being the pressure in baryes, k the Boltzmann constant, 1.371×10^{-16} erg. deg.$^{-1}$, m the mass of an atom in the gas and M the atomic or molecular weight of the gas on the basis of O = 16.

The factor $\alpha_0 (1 - \theta)$ is the fraction of the incident atoms which condense, α_0 being a numerical factor not exceeding unity, which measures the efficiency of the condensation on a *bare surface.*

For a steady state the rates of condensation and evaporation are equal. Equating them and solving for θ we have

$$\theta = \frac{\alpha_0\mu}{\nu_1 + \alpha_0\mu} \qquad (2)$$

The average life of τ of an adsorbed atom on the surface is

$$\tau = \sigma_1/\nu_1 \qquad (3)$$

where σ_1 is the number of adsorbed atoms per unit area for a saturated surface, $\theta = 1$. Thus equation (2) may also be written

[1] I. Langmuir, THIS JOURNAL, 40, 1361 to 1403 (1918).

[2] The word molecule properly includes the atom. However, in the applications of the theories developed in this paper, we shall deal principally with adsorption of atoms such as cesium and therefore for brevity shall use the word atom. In most cases the statements will be valid if atom is replaced by molecule.

$$\Theta = \frac{\alpha_0 \tau \mu}{\sigma_1 + \alpha_0 \tau \mu} \tag{4}$$

This equation has been found to apply, with reasonable accuracy, to a surprisingly large number of cases of adsorption on plane surfaces. Considering the nature of the simplifying assumption made in its derivation, it should, of course, not be looked upon as a general equation of the "adsorption isotherm."

Several recent quantitative studies of adsorption phenomena in this Laboratory have given, as expected, data on evaporation and condensation which are very different from those indicated by Eqs. (2) or (4). It therefore seems desirable to present a more up-to-date analysis of the factors determining the rates of evaporation and condensation and to derive equations giving the amount of adsorbed gas, taking into account the effect of the forces acting between adjacent adsorbed atoms.

The evaporation of adsorbed atoms or adatoms from a surface must be governed by laws very similar to those that apply to homogeneous solids and liquids.

Vapor Pressures of Liquids.—The vapor pressures of solids and liquids or their rates of evaporation in vacuum depend principally upon the heats of evaporation since at least approximate values of the latent heats can be calculated from the boiling points by such rules as Trouton's rule. In general the vapor pressure is given with considerable accuracy over a wide range of temperature by an equation of the type

$$p = AT^{\gamma}\epsilon^{-b/T} \tag{5}$$

which is analogous to the Richardson equation for electron emission.

The curve obtained by plotting $\ln p$ against $1/T$ is a straight line if $\gamma = 0$. If γ differs from zero the line must be curved, but because of the very rapid increase of p with T, the range of temperature over which p can be observed is usually so limited that the curvature is extremely small, if not wholly imperceptible. For example, by measurements of electron emission it has not been possible to decide whether $\gamma = 0.5$ or 2.

Thus within a limited range extending symmetrically above and below a mean temperature T_M, we can always replace Eq. (5) by

$$p = A_0\epsilon^{-b_0/T} \tag{6}$$

by so choosing A_0 and b_0 that the two equations give at $T = T_M$ not only the same value of p but the same slope dp/dT. Under these conditions we have

$$A_0 = AT_M^{\gamma}\epsilon^{\gamma} \text{ and } b_0 = b + \gamma T_M \tag{7}$$

The slope of the $(\ln p)$ *vs.* $(1/T)$ curve from Eq. (6) is constant, $S_0 = -b_0$, while that obtained from Eq. (5) is variable and at any point has the value

$$S = S_0 + \gamma(T - T_M) \tag{8}$$

A series expansion of the equation obtained by dividing Eq. (5) by Eq. (6) shows that

$$\ln \frac{p}{p_0} = (\gamma/2) \left(\frac{T - T_M}{T_M} \right)^2 \qquad (9)$$

where p and p_0 are the values of p given by Eqs. (5) and (6), respectively, after choosing the constants in accord with Eq. (7).

The temperature change $\Delta T = T - T_M$ needed to cause a 5% change in p is

$$\Delta T = 0.05\ T^2/b_0$$

With $T = 800$ and $b_0 = 32{,}000$, which are typical experimental data such as we shall have occasion to use in studies of cesium films on tungsten, it is thus necessary to know the filament temperatures within 1° in order to get p within 5%.

By Eq. (9) we see that Eqs. (5) and (6) give values of p agreeing within 5% as long as $(T - T_M)/T_M$ is numerically less than $0.32\ \gamma^{-1/2}$. With $\gamma = 2$ and $T_M = 800$ there is thus a range of temperature extending about 180° on each side of T_M in which Eqs. (5) and (6) are experimentally indistinguishable if temperatures can only be measured within 1°. Over this total range of 360°, p increases more than 10^8-fold.

According to the Clapeyron equation and the laws of ideal gases, λ, the latent heat of evaporation per atom, at constant pressure is

$$\lambda = -k \frac{\mathrm{d} \ln p}{\mathrm{d}(1/T)} = kb_0 = k(b + \gamma T) \qquad (10)$$

The exponent γ is thus a measure of the temperature coefficient of λ and the constant A may be regarded as the integration constant of the Clapeyron equation.

Le Chatelier pointed out long ago[3] that the integration constants of the Clapeyron equation for reactions of the same type have approximately the same numerical value.

Trouton's rule states that L, the latent heat in calories per gram molecule, is proportional to the boiling point T_B. The value of the ratio L/T_B from data on ordinary liquids is usually given as 20.7. Examination of Eq. (6) shows that Trouton's rule follows from this equation at once if A_0 is a universal constant. Placing $p = 10^6$ baryes (1 atmosphere) and $b_0/T = 20.7/R = 10.4$, we obtain $A_0 = 3.4 \times 10^{10}$ baryes.

When Trouton's rule is applied to substances having very low or very high boiling points, it is soon seen that L/T_B varies considerably and in general is higher for substances having higher boiling points.

Hildebrand[4] has reasoned that different substances should be compared, not at their boiling points, T_B, but at temperatures T_0 at which the liquids have the same vapor concentration.

[3] See H. S. Taylor, "Treatise on Physical Chemistry," Van Nostrand Co., N. Y., 1924, Vol. II, p. 1135.

[4] J. H. Hildebrand, THIS JOURNAL, **37**, 970 (1915); **40**, 45 (1918).

Replacing p by its value nkT, in terms of the atomic concentration n, and putting $\lambda = kb_0$, Eq. (6) becomes

$$n = (A_0/kT)\epsilon^{-\lambda/kT} \tag{11}$$

Hildebrand's rule states that if, for each of a series of substances, we chose a temperature T_0 which gives the vapor of that substance an arbitrary concentration n_0 (the same for all), then the ratio λ/T_0 is the same for all the substances. By Eq. (11) this must mean that A_0/kT_0 is also the same for all the substances. Thus instead of A_0 being constant, as it should be by Trouton's rule, Hildebrand's rule requires that A_0 shall be proportional to T_0, so that in Eq. (6) we can replace A_0 by CT_0 where C is a universal constant. We may now get rid of T_0, a troublesome arbitrary factor, by transforming the equation by means of Eq. (7), obtaining ($\gamma = 1$)

$$p = A_1 T\epsilon^{-b_1/T} \tag{12}$$

where A_1 is a universal constant having the value C/ϵ and

$$b_1 = b_0 - T_0 \tag{13}$$

This conclusion from Hildebrand's rule is not strictly in accord with the Clapeyron equation since by Eq. (10) b_1 must have the value

$$b_1 = b_0 - T = (\lambda/k) - T \tag{14}$$

The errors made by replacing T by T_0 are, however, far less than those due to other causes of variability of the "universal constant" A_1. The experimental evidence in support of Hildebrand's rule is thus equally good evidence that the constant A_1 in Eq. (12) is approximately the same for all substances. This formulation of Hildebrand's rule has the advantage that it does not involve any arbitrarily selected standard concentration such as that needed to define T_0.

When a liquid or solid is in equilibrium with its vapor, evaporation and condensation go on simultaneously. In general every incident atom condenses, so that $\alpha = 1$ and the rate of condensation μ is given by Eq. (1); this must also equal the rate of evaporation ν_1. The average life τ of the atoms on the surface, as given by Eq. (3), can thus be expressed by

$$\tau = (2\pi mkT)^{1/2}\sigma_1/p \tag{15}$$

The velocity constant K of a monomolecular reaction varies with temperature according to the equation

$$K = K_0\epsilon^{-b/T} \tag{16}$$

Dushman[5] calls attention to the fact that K_0 has the dimensions of a frequency. The constant b may also be related to a frequency ν_b by the Einstein equation $b = h\nu_b/k$. Dushman makes the hypothesis that these two frequencies are the same, $K_0 = \nu_b$. Let us generalize this hypothesis by assuming that

$$K_0 = \beta\nu_b \tag{17}$$

where β is a numerical factor which Dushman takes equal to unity.

[5] S. Dushman, THIS JOURNAL, **43**, 397 (1921).

The average life τ of a reacting molecule is $\tau = 1/K$. We may thus apply Eq. (16) to evaporation by identifying this average life with that of an atom on the surface of an evaporating substance. From Eqs. (16) and (17) we obtain

$$\tau = (h/\beta bk)\epsilon^{b/T}$$

or

$$\tau = 4.8 \times 10^{-11}\,(1/\beta b)\epsilon^{b/T} \text{ seconds} \tag{18}$$

Elimination of τ from Eqs. (15) and (18) gives[6]

$$p = (\beta b\sigma_1 k/h)(2\pi mkT)^{1/2}\,\epsilon^{-b/T} \tag{19}$$

The value of σ_1 depends primarily on the atomic volume but also on the arrangement of the atoms of the solid or liquid. For a crystal having a body-centered cubic lattice, such as tungsten, the crystal faces having closest packing of the atoms are the dodecahedral faces (110) and for these

$$\sigma_1 = 0.897\,(\rho/m)^{2/3} = 6.43 \times 10^{15}\,(\rho/M)^{2/3} \tag{20}$$

where ρ is the density of the solid. The shortest distance δ_0 between atoms is

$$\delta_0 = 1.091\,(m/\rho)^{1/3} = 1.289 \times 10^{-8}\,(M/\rho)^{1/3} \tag{20a}$$

With a close-packed lattice (face-centered) the octahedral faces contain most atoms per unit area and σ_1 is given by an equation like (20) having a coefficient 0.916 instead of 0.897. The coefficient for the expression for δ_0 is 1.122 instead of 1.091. Even for liquids we may use Eq. (20) with sufficient accuracy.

By substituting this value of σ_1 in Eq. (19) and by introducing numerical values of the constants, we obtain as a general equation for vapor pressure

$$p = 5.1 \times 10^6 \beta b\rho^{2/3} M^{-1/6} T^{1/2}\,\epsilon^{-b/T} \tag{21}$$

where

$$b = b_0 - (1/2T) \tag{22}$$

We now have three equations, (6), (12) and (21), which should give p in terms of b. Let us test them by the data on vapor pressures in "International Critical Tables" (I. C. T.), Volume III. In most cases the tables contain the constants B and A_c in the equation

$$\log_{10} p_{\text{mm.}} = 0.05223\,A_c/T + B \tag{23}$$

together with the range in temperature over which this relation is known to hold. Comparing this equation with Eqs. (6), (12), (21) and (7) we find that

$$\log A_0 = B + 3.125 \tag{24}$$
$$\log A_1 = B - \log T_M + 2.690 \tag{25}$$
$$\log \beta = B - \log (b\rho^{2/3} M^{-1/6}) - (1/2)\ \log T_M - 3.80 \tag{26}$$
$$b_0 = -0.1203\,A_c \tag{27}$$

[6] This equation, with $\beta = 1$, has already been tested by Dushman and Langmuir. See Dushman's chapter in H. S. Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924 ed., Vol. II, pp. 1041–1042.

In the case of substances for which B is not given in I. C. T., we may calculate B from two fairly widely separated values of vapor pressure (in mm.) by the equation

$$B = (T_1 \log p_1 - T_2 \log p_2)/(T_1 - T_2) \qquad (28)$$

Table I contains values of B and b_0 for eighteen chemical elements, selecting those for which the vapor pressure data are probably of greatest accuracy. The second column gives T_M, the mid-point of the temperature range covered by the data which were used in calculating the values of B and b_0 in the third and fourth columns. All these data were obtained from I. C. T. except in the case of rubidium and cesium. The positive ion method[7] developed in this Laboratory is believed by the writer to be far more accurate than other published data for these two elements.

If Trouton's rule is valid, the values of A_0, and therefore by Eq. (24) the values of B, should be the same for all substances. At the bottom of the table the average value of B is given and also the "standard deviation" (S. D.) of the individual values from the mean, *viz.*, the root-mean-square deviation. The average value of $\log A_0$ is therefore 10.65 with a S. D. of 1.19.

The fifth column gives the $\log A_1$ calculated from B by Eq. (25). These data serve as a test of Hildebrand's rule. The S. D. from the average value is only 0.52, which is less than half of that observed with Trouton's rule.

TABLE I

VAPOR PRESSURE DATA OF COMMON ELEMENTS

1	2 T_M	3 B	4 b_0	5 $\log A_1$	6 $\log \beta$	7 $\log A_{1.5}$
He	4.0	4.65	17.3	6.74	+0.03	6.22
H_2	19.3	5.48	122	6.88	− .20	6.02
N_2	75	6.86	709	7.68	− .41	6.52
O_2	79	7.09	872	7.88	− .38	6.72
A	88	6.96	821	7.71	− .54	6.52
Kr	114	6.92	1,130	7.55	− .84	6.31
Cl_2	221	7.59	2,580	7.94	− .57	6.55
Br_2	293	7.88	3,810	8.10	− .68	6.65
I_2	423	7.98	5,370	8.04	− .90	6.51
P_4	373	7.80	6,260	7.92	− .89	6.42
Hg	470	7.90	7,260	7.92	−1.45	6.36
Cd	700	8.16	12,500	8.00	−1.43	6.36
Zn	790	8.18	14,300	7.97	−1.48	6.31
Na	600	7.55	12,400	7.46	−1.48	5.86
Rb	340	7.43	9,500	7.59	−1.40	6.11
Cs	320	7.53	9,200	7.71	−1.31	6.25
C	4400	9.60	65,000	8.65	−0.87	6.61
W	2800	9.92	108,000	9.16	−1.11	(7.22)
Average		7.53		7.83	−0.88	6.37
S. D.		±1.19		±0.52	±0.46	±0.22

[7] Langmuir and Kingdon, *Proc. Roy. Soc.* (London), [A] **107**, 61 (1925); Killian, *Phys. Rev.*, **27**, 578 (1926).

The data of the sixth column, which serve as a test for the validity of Eq. (21), show that the average value of $\log \beta$ is -0.88 and the individual values have an S. D. of 0.46. Thus if we place $\beta = 0.13$ in Eq. (21) we have an expression for vapor pressure which is more accurate than Eq. (12). By Dushman's hypothesis β should be unity; the observed value is of about the same order of magnitude although distinctly less than unity.

In some preliminary tests of Eq. (21), $\log \beta$ was calculated from Eq. (26), by using approximate values of b from Trouton's rule placing $b = 11.5\, T_B$. This gives a term $(3/2) \log T_M$ instead of $(1/2) \log T_M$. The resulting equation was found to agree with the experimental data much better than does Eq. (21). Furthermore, it was observed that the factor $\rho^{2/3}\, M^{-1/6}$ did not contribute materially to this accuracy. It was therefore decided to test also the empirical equation

$$p = A_{1.5} T^{3/2}\, \epsilon^{-b/T} \tag{29}$$

where

$$b = b_0 - (3/2)T = (\lambda/k) - (3/2)T \tag{30}$$

to see if $A_{1.5}$ is not more nearly constant than A_1 or β. The data in the seventh column[8] were thus calculated, in accord with Eqs. (7) and (23), from

$$\log A_{1.5} = B - (3/2) \log T_M + 2.473 \tag{31}$$

It is seen in fact that the S. D. of $\log A_{1.5}$ is now only 0.22, which is only about one-third as great as the S. D. for $\log A_1$ and less than one-half that of $\log \beta$. The average value corresponds to

$$A_{1.5} = 2.5 \times 10^6 \text{ baryes deg.}^{-3/2} \tag{32}$$

The data on the vapor pressures of liquid chemical compounds in I. C. T., Vol. 3, pp. 213–214, are in agreement with these conclusions. Certain "associated" substances, such as H_2O and NH_3 give values A_1 and $A_{1.5}$ about ten times above normal. The following ten liquids, for which accurate data are available, give $\log A_{1.5} = 6.50 \pm 0.16$: HCl, HBr, HI, CCl_4, CS_2, $SiCl_4$, $SnCl_4$, C_2H_6, C_4H_{10}, C_6H_6 (benzene). The data for fused salts are similar, although naturally less reliable. Thus the seven salts: $PbCl_2$, $HgCl_2$, LiCl, NaCl, KCl, KI, LiF, give $\log A_{1.5} = 6.43 \pm 0.47$, the mean value of T_M being 1340°K.

We may thus conclude that Eq. (29) with the value of $A_{1.5}$ given by Eq. (32) is the most accurate of the expressions we have tested, giving the vapor pressures of liquids usually within about 40%, if the value of b_0 is known.[9]

[8] In forming the average, the value for W was discarded as this metal was in the *solid* state. The data for C are said in I. C. T. to apply to liquid carbon.

[9] These deviations from Eq. (29) are of course not to be regarded as errors. Any rigorous calculation of vapor pressures must involve either knowledge of specific heats and chemical constants or a detailed knowledge of the constitution of the liquid and gas phase such as we may hope to obtain from spectroscopic data, etc. This knowledge is so seldom available that it is a matter of considerable *practical importance* to have an empirical equation like Eq. (29) which is so generally applicable.

Vapor Pressures of Solids.—If the latent heat of fusion L_F is known, the vapor pressure of a solid below the melting point T_F may be calculated from that of the liquid above this temperature. Thus we have

$$P_S = A_S T^\gamma \exp.(-L_S/RT) \text{ and } p_L = A_L T^\gamma \exp.(-L_L/RT)$$

Equating $p_S = p_L$ at T_F and noting that $L_S - L_L = L_F$ we have

$$A_S = A_L \exp.(L_F/RT_F) \tag{33}$$

The heats of fusion of twenty-one metallic elements are given in I. C. T., Vol. II, p. 458. The ratio L_F/T_F, which we shall call f, is approximately constant, the average value for all these elements (except Sb, which gives 5.3) being 2.34 calories per g. atom per degree, while the S. D. of the individual values is ± 0.72. For the non-metallic elements (I. C. T., Vol. V, p. 131), taking L_F as the heat of fusion per gram molecule, we find that the ratio $f = L_F/T_F$ is about 2.3 for A, O_2, H_2, N_2 and P_4, but rises to about 9.7 for Cl_2 and Br_2.

Among compounds such as HCl, CCl_4, C_6H_6, NaCl, which have rather compact molecules, f has values ranging from 3 to 8, but for organic substances consisting of large molecules such as stearic acid and tristearine, f rises to large values (40 and 124, respectively), increasing roughly in proportion to the number of atoms in the molecule.[10]

Equation (33), after putting $R = 2$ calories, thus becomes

$$\log A_S = \log A_L + 0.218 f \tag{34}$$

We may thus apply Eq. (29) to the vapor pressures of solids if we increase the value of $A_{1.5}$ in accord with Eq. (34). For solid elementary substances or those having relatively rigid molecules, we may put $f = 2.3$ and thus the value of $A_{1.5}$ instead of being given by Eq. (32) should be

$$\text{(for solids) } A_{1.5} = 8 \times 10^6 \text{ baryes deg.}^{-3/2} \tag{35}$$

Chlorine and bromine having less rigid molecules give values of $f = 9.7$ so that by Eq. (34) the value of $A_{1.5}$ for these substances in solid form is about 150 times as great as for ordinary liquids. This agrees well with the

[10] These large values of f are understandable when we consider that a large part of the heat of fusion of such substances must represent an *internal* heat of fusion of the molecules themselves which would increase roughly in proportion to the size of the molecule. Thus in solid tristearine the three hydrocarbon chains are undoubtedly rigidly arranged within the solid lattice so that the molecule itself is solid. But when the substance melts, the molecule also melts.

With such large molecules it is probable that the *molecules of the vapor* may also exist in two states in which they are internally solid or liquid; however, the transition will probably occur in a temperature range far below the melting point of the solid phase. In this range the specific heat of the vapor would have abnormally high values.

From this point of view the large increase in A observed with some solids is due to the fact that the molecules "melt" during the evaporation process so that the vapor molecules have an internal mobility not possessed by those in the solid. If the molecules evaporated as solid molecules, f would have a normal value but the heat of sublimation L_S would no longer be equal to the sum $L_L + L_F$.

data of I. C. T. on the vapor pressures of these solids. For example, for solid chlorine B is given as 9.95, while for liquid chlorine (see Table I) it is 7.59. For organic substances such as tristearine ($f = 124$) according to Eq. (34) $A_{1.5}$ must rise to the enormous value of 10^{33}.

We may thus conclude that $A_{1.5}$ in Eq. (29) may be regarded approximately as a universal constant as applied to liquids and as another constant when applied to solids having rigid molecules; but for other solids the values of $A_{1.5}$ may increase to very much larger values.

Evaporation of Adsorbed Atoms.—The average life τ of an atom on the surface of an evaporating liquid or solid was given by Eq. (15) in terms of σ_1 and p. Disregarding for the present solids with non-rigid molecules, we may consider that p can be expressed in accord with Eq. (29) as a function of T and b. In this way a general expression for τ can be derived

$$\tau = (2\pi mk)^{1/2}(A_{1.5}T)^{-1}\sigma_1\epsilon^{b/T} \tag{36}$$

or if we put $A_{1.5} = 8 \times 10^6$ by Eq. (35)

$$\tau = 4.7 \times 10^{-27} M^{1/2}\sigma_1 T^{-1}\epsilon^{b/T} \tag{37}$$

The atoms of solids and liquids as well as gases have kinetic energies corresponding approximately to $(3/2)kT$, so that their average velocity v may be taken to be $1.45 \times 10^4(T/M)^{1/2}$. It is of interest to know δ, the average total distance measured along its path, which the surface atom travels in the time τ, so that we may estimate the number of oscillations that occur during its life τ. Putting $\delta = v\tau$ and combining with Eqs. (37), (20) and (20a), we thus obtain

$$\delta/\delta_0 = 34(\rho/M)\ T^{-1/2}\epsilon^{b/T} \tag{38}$$

where b is given by Eq. (30).

It should be noted that the coefficient of $\epsilon^{b/T}$ is of the order of magnitude of unity. Thus at very high temperatures or for very small values of b (b/T small), δ becomes approximately equal to δ_0, so that the atoms evaporate in the time necessary to perform one oscillation. Under such conditions we may hardly consider that an impinging molecule condenses and reëvaporates.

We need to examine a little more closely the meaning of τ and σ_1. The life τ may be called the *evaporation life;* a diffusion of a surface atom into the interior of a liquid should not be regarded as a termination of its life. More rigorously τ may be defined by stating that dt/τ is the probability that a given surface atom will evaporate in the time dt.

We have seen that Eq. (29), with the appropriate values of $A_{1.5}$, is applicable with reasonable accuracy to the evaporation of atoms or molecules from surfaces of such widely different types as those of liquid helium, phosphorus, mercury or carbon.

The life of any atom on the surface thus depends essentially on the value of b, in accord with Eqs. (36) and (37). In general, with homogeneous

bodies, the heat of evaporation ($\lambda = kb_0$) is the same for all the atoms. If there are on the surface atoms of more than one kind which differ in composition or in their geometrical relation to one another, the values of b for different atoms may vary. This should not affect the validity of Eq. (36); it would merely give a separate value of τ for each atom dependent upon the b for that atom. Since it is very unlikely that the validity of this equation requires that the evaporating atoms shall be similar to those in contact with them on the surface, we are justified in applying Eqs. (36) and (37) to adsorbed films.

Adjacent adsorbed atoms may exert strong forces on one another, but this will produce its effect on τ, in accord with Eq. (36), by the change in the value of b. However, if the surface is homogeneous, we may take the same value of b for all the adsorbed atoms, although b will vary with the surface concentration σ because of the forces between adatoms. In the following discussions we postulate homogeneous surfaces, but in a later section shall treat the case of heterogeneous surfaces where b varies from atom to atom, not because of the interactions of adatoms, but because of non-uniform forces exerted by the underlying surface.

Consider now a homogeneous surface on which there is an adsorbed film containing σ atoms per unit area, the value of τ being the same for all atoms. The rate of evaporation (atoms cm.$^{-2}$ sec.$^{-1}$) is proportional to the probability per sec. $(1/\tau)$ for the evaporation of each atom, so that

$$\nu = \sigma/\tau = \sigma_1\Theta/\tau \tag{39}$$

Taking the value of τ from Eq. (36) we have

$$\nu/\Theta = A_{1.5}(2\pi mk)^{-1/2}T\epsilon^{-b/T} \tag{40}$$

or, after inserting numerical values including $A_{1.5} = 8 \times 10^6$ from Eq. (35) and transforming by Eq. (7), we have

$$\nu/\Theta = 5.7 \times 10^{26}M^{-1/2}T_M\epsilon^{-b/T} \tag{41}$$

where

$$b = b_0 - (1/2)T \tag{42}$$

In deriving these equations for the evaporation of adatoms we have not needed to assume that Θ is small or that the interactions between the adatoms are negligible. These relations should thus be applicable to concentrated as well as to dilute adsorbed films. Since, however, b is in general a function of Θ, it does not follow from Eq. (40) that ν is proportional to Θ, except at such low values of Θ that b is close to the limiting value that it must approach as Θ becomes zero.

It is frequently of interest to know the relation between Θ and the gas pressure p in equilibrium with an adsorbed film. Since the rates of condensation and evaporation are then equal we may put

$$\nu = \alpha\mu \tag{43}$$

By combining Eqs. (40), (43) and (1) we obtain the useful result.

$$p = (\Theta/\alpha)A_{1.5}T^{3/2}\epsilon^{-b/T} \tag{44}$$

which becomes identical with Eq. (29) if $\Theta = 1$ and $\alpha = 1$. After inserting numerical values according to Eq. (35) and transforming by Eq. (7), this becomes

$$\Theta = 2.8 \times 10^{-8}\, \alpha p T_M^{-3/2} \epsilon^{b/T} \qquad (45)$$

Comparison with Experimental Data

In studies of the electron emission of thoriated tungsten filaments,[11] the rate of evaporation of adsorbed thorium atoms over the temperature range from 2055 to 2450°K. and at an average value $\Theta = 0.5$ was found to be given by

$$\log \nu = 31.43 - 44{,}500/T$$

By Eq. (41), putting $M = 232$, $T_M = 2250$ and $\Theta = 0.5$, we obtain

$$\log \nu = 28.62 - b/2.3T$$

The difference of 2.8 between 31.43 and 28.62 is far greater than the S. D. of 0.2 in $\log A_{1.5}$ which we found in Table I. This does not necessarily indicate, however, that the accuracy of Eq. (41) as applied to evaporation of adsorbed substances is not comparable with that of Eq. (29) for vapor pressures. If we put

$$\log \nu = 29 - 39{,}000/T$$

we find that these values of $\log \nu$ agree, with a S. D. of 0.12, with those experimentally determined. This S. D. is certainly within the possible experimental error.

Measurements[12] of the rates of evaporation of adsorbed oxygen atoms from a tungsten surface have given the data in Table II.

TABLE II

THE RATES OF EVAPORATION OF OXYGEN ATOMS FROM A TUNGSTEN SURFACE

T	$t_{1/2}$, min.	$\log (\nu/\Theta)_{obs.}$	$\log (\nu/\Theta)_{calcd.}$	Diff.
1856	27.5	11.77	11.82	−0.05
1978	2.00	12.91	(12.91)	(0.0)
2070	0.292	13.75	13.64	+0.11

The time in minutes required to evaporate half of the adsorbed oxygen is shown in the second column. The *ratios* of these values are far more accurate than the absolute values. Converting these times to seconds and dividing by ln 2 we get τ, and then we may calculate $\nu/\Theta = \sigma_1/\tau$ according to Eq. (39). Since oxygen atoms or ions are smaller than tungsten atoms and are held by extremely strong forces, we may take σ_1 to be the same as for the tungsten atoms on the surface, $\sigma_1 = 1.42 \times 10^{15}$. This gives the values under $(\nu/\Theta)_{obs.}$ in the table. In these experiments Θ varied in a range between 0.3 and 0.1.

Putting $M = 16$ and $T_M = 2000$ in Eq. (41) and choosing b so that the value of ν/Θ at 1978° agrees with that observed, we obtain

$$\log (\nu/\Theta) = 29.45 - 32{,}720/T \qquad (46)$$

[11] Langmuir, *Phys. Rev.*, **22**, 357 (1923). See Table VI and Eq. (41) on p. 391.

[12] Langmuir and Villars, THIS JOURNAL, **53**, 495 (1931).

and from this equation the values of log $(\nu/\Theta)_{\text{calcd.}}$ were calculated. Table II shows that the agreement is within the probable experimental error, as the S. D. corresponding to the differences is only 0.07. The value of b_0 by Eqs. (42) and (46) is 76,400, and the heat of evaporation per gram atom b_0R is 152 kg. cal., which is to be compared with 162 obtained[12] from the temperature coefficient of $t_{1/2}$.

The adsorption of oxygen on tungsten calls into play powerful chemical forces which are often regarded as very different in type from those involved in the evaporation of such substances as are listed in Table I. It is therefore of particular interest to find that Eq. (40) applies so well to a case of this kind.

Forces Acting on Adatoms.—There are two types of forces to be considered: those exerted by the underlying atoms, and those acting between the adatoms.

The underlying atoms always exert attractive forces but these may have an enormous range of intensities. If the surface is covered with adatoms having a heat of evaporation $\lambda = kb_0$, the energy per unit area which must be expended to remove them is $\sigma_1 kb_0$. If the effective range of the forces is 10^{-8} cm., the force per unit area which must be exerted to pull them off is thus $10^8\sigma_1 kb_0$. With an oxygen film on tungsten $b_0 = 76{,}000$ and $\sigma_1 = 1.4 \times 10^{15}$, so that this force corresponds to 10^{12} baryes or 10^6 atmospheres.

The smallest forces that are likely to occur are those involved when helium atoms or hydrogen molecules strike a chemically saturated surface such as that of tungsten covered by adsorbed oxygen. In such cases[13] there is no appreciable adsorption and the incident atoms remain on the surface for a time so short that they do not even reach thermal equilibrium, so that the accommodation coefficient is much less than unity (0.1 to 0.2).

The stability of an adsorbed film depends primarily on the magnitude of b_0 and on the pressure in the gas phase. The condition under which an approximately complete monatomic film is in equilibrium at the pressure p can be found by putting $\Theta = 1$ in Eq. (45)

$$\alpha p e^{b_0/T} > 3.6 \times 10^7 \, T_M^{3/2} \qquad (47)$$

We shall see later in most cases that $\alpha = 1$ except when Θ approaches closely to unity. Thus under high vacuum conditions when $p = 1$ barye, the surface will be completely covered only when b_0/T exceeds 25.9 or 28.6 at values of T_M of 300 or 2000°, respectively. At atmospheric pressure ($p = 10^6$), the corresponding values of b_0/T are 12.1 and 15.2. From these data we find, for example, that an oxygen film in presence of 1 barye of oxygen should cover a tungsten surface ($b_0 = 76{,}000$) up to about 2600°K.; this conclusion is in accord with experiments.[14] A filament at room

[13] Blodgett and Langmuir, *Phys. Rev.*, **40**, 78 (1932).

[14] Langmuir, THIS JOURNAL, **38**, 2271 (1916).

temperature in presence of gas at 1 barye would be covered if b_0 exceeds 7000.

When b_0/T is so large that the first layer of adatoms is nearly complete, it is possible that a second layer may form; let Θ_2 be the fraction of the surface covered by this second layer.

The conditions under which Θ_2 becomes comparable with unity are given, as before, by Eq. (47) if we replace b_0 by b' which measures the heat of evaporation of atoms from the second layer. There are now two important cases to consider according as b' is less than or is greater than b_0.

Case I, $b' < b_0$.—There will be a range of temperature in which the film will be a complete monatomic film. For example, with a gas pressure of 1 barye and a temperature range in the neighborhood of $T_M = 600°$, Eq. (47) shows that a complete film forms if b/T exceeds about 27. The temperature T_1 at which the first layer becomes complete is thus $T_1 = b_0/27$, whereas the second layer becomes complete at $T_2 = b'/27$. If $b_0 = 20{,}000$ and $b' = 15{,}000$, we have $T_1 = 740$ and $T_2 = 555°$. By Eq. (45) we calculate that at 740° where the first layer is complete, $\Theta_2 = 0.0012$. The temperature coefficients are so great that above 740° the value of Θ in the first layer decreases to 0.14 at 800 and 0.01 at 900°; in the second layer Θ_2 increases to 0.019 at 650°, 0.13 at 600° and 1.0 at 555°.

Thus even when b' is as great as 0.75 b_0, the monatomic character of the adsorbed film is very striking, and there is a range of about 100° in which the film is complete.

Let us consider some typical cases in which $b' < b_0$.

The forces between tungsten atoms in solid tungsten (roughly measured by $b_0 = 108{,}000$ as given in Table I) are comparable in magnitude with those holding the atoms in the most stable of chemical compounds. These forces at a clean tungsten surface are very much unsaturated, each atom having only 6, instead of 8, neighbors. Although in other solids the forces are less intense than in tungsten, comparison with Table I shows that b_0 for typical solids will be at least as great as 10,000.

When gas molecules such as H_2, N_2 or O_2, or even inert gas atoms He or A, are brought into contact with the clean surface of solid bodies, attractive forces must usually come into play which are much larger than those holding these gas molecules on surfaces of their own liquid phases. Such attraction would result merely from the polarization of the molecules produced by their deformation in a strong field of force,[15] but these "molecular" forces will never rise to very high values.

At sufficiently low temperatures in presence of gas the surfaces of solids must become completely covered with adsorbed films. Additional gas

[15] A discussion of the nature and magnitude of such forces was given in a paper "Forces Near the Surfaces of Molecules," I. Langmuir, *Chem. Rev.*, **6**, 451 (1929); see particularly pp. 457–462.

molecules striking such surfaces are acted on only by the weak forces exerted by the adsorbed molecules and not the strong forces characteristic of the solid and therefore in all such cases $b' < b_0$.

An estimate of the magnitude of b_0 involved in typical molecular adsorption on non-metallic surfaces may be made from measurements[16] of the adsorption of gases on plane surfaces of glass and mica at the temperature of liquid air.

The amount of gas adsorbed by a given surface was found to vary with the pressure p in accord with the equation

$$q = abp/(1 + ap) \tag{48}$$

where a and b are constants at any given temperature. The parameter a has the dimensions of the reciprocal of a pressure and its value does not depend upon the amount of surface exposed nor upon the units used in measuring q and b. Comparison of Eq. (48) with Eq. (4) shows that they are of the same form and that

$$ap = \alpha_0 \tau\mu/\sigma_1$$

Combining with Eqs. (43), (39) and (44)

$$1/a = p/\Theta = (1/\alpha)A_{1.5}T^{3/2}\epsilon^{-b/T} \tag{49}$$

where b is given by Eq. (30).

For argon, oxygen and nitrogen at 90°K. in contact with dry glass the values of a were found to be 0.051, 0.079 and 0.088 (baryes)$^{-1}$. The adsorption of these gases on mica gave 0.065, 0.080 and 0.156. From Eqs. (49), (35) and (30), putting $\alpha = 1$, we obtain values of b_0 that average 1950 with a S. D. of only ±27.

Table I shows that the average b_0 for the evaporation of these gases is 800. Thus the heat of evaporation of these adsorbed molecules from glass or mica surfaces is about 2.4 times as great as from the corresponding liquid phases.

In the experiments referred to, pressures from 1 to 100 baryes were used. At somewhat higher pressures or lower temperatures the adsorbed films approached saturation ($\Theta = 1$). The forces tending to hold molecules in a second layer are probably not appreciably greater than those that would act in the liquid phases of these gases. It is true that the adsorbed molecules in the first layer are not wholly in the condition of normal molecules in the liquid phase; they are polarized by deformation in a strong field of force. But surely the forces they exert on molecules in the second layer are much closer to the forces characteristic of gas molecules than they are to the forces exerted by the underlying solid upon the molecules in the first layer.

Transmission of Polarization through Molecular Layers.—The forces acting between successive layers of molecules may be characterized

[16] Langmuir, THIS JOURNAL, **40**, 1361 (1918). See particularly Eq. (31) and the Tables on pp. 1390–1391.

by a series of values of b such as b_0, b', b''. These must rapidly approach a limiting value b_∞ which would be the same as for a condensed phase of the adsorbed material. Almost the whole of the transition from b_0 to b_∞ must occur between b_0 and b'.

The experiments of de Boer[17] on the adsorption of iodine vapor on solid films of calcium fluoride enable us to estimate the magnitude of these transmitted effects. His experimental results, in terms of our nomenclature, may be summarized by the equation

$$\log [-\log(p/1.1\ p_0)] = -4.3 \times 10^{-16}\ \sigma_1 n + 0.43 \qquad (50)$$

where n is the number of layers of molecules of I_2, each layer containing σ_1 molecules per sq. cm.; p is the pressure of iodine vapor in equilibrium with the film at a given temperature (*ca.* 20°), while p_0 is the vapor pressure of solid iodine at the same temperature. In the experiments p/p_0 was varied only between 0.1 and 0.95.

De Boer and Zwikker[18] have calculated that in a series of layers of polarizable molecules the polarization in the $(n+1)^{st}$ layer is K_1 times that in the nth, where K_1 is a constant numerical factor less than unity, but which is proportional to the polarizability α of the molecules. From this they obtain an expression for the vapor pressure, which we may put in the form

$$p = K_3 p_0 \exp.\ (K_2 K_1^n) \qquad (51)$$

Although de Boer does not give the numerical value of K_1, comparison of Eqs. (50) and (51) shows that

$$\log K_1 = -4.3 \times 10^{-16}\sigma_1;\ K_2 = -6.2;\ K_3 = 1.1 \qquad (52)$$

Assuming that the arrangement of atoms in the CaF_2 film (produced by evaporation) is like that of octahedral faces of a fluorite crystal, de Boer calculates that the number of fluorine ions per sq. cm. is 7.75×10^{14}. He considers that this number of iodine atoms per unit area are adsorbed. Applying Eq. (20) to molecular iodine we obtain $\sigma_1 = 4.56 \times 10^{14}$ molecules cm.$^{-2}$.

Harris, Mack and Blake[19] have shown that iodine crystals belong to the orthorhombic system and that the atoms are grouped in pairs as molecules. The distances between the centers of the two atoms in a molecule is 2.79 Å., while the shortest distance between the centers of atoms which are not in the same molecule is 3.51 Å. The unit cell of dimensions $a = 4.795$ Å., $b = 7.255$ Å. and $c = 9.780$ Å., contains four molecules whose centers are at the corners and at the centers of the faces.

From these data we find that in crystal faces parallel to two axes the values of σ_1 are: for *ab* 5.75, for *bc* 2.82 and for *ca* 4.26 (unit = 10^{14} mole-

[17] J. H. de Boer, *Z. physik. Chem.*, [B] **13**, 134 (1931); *Proc. Acad. Amsterdam*, **31**, 906 (1928); see particularly the equation at top of p. 152.

[18] J. H. de Boer and C. Zwikker, *Z. physik. Chem.*, [B] **3**, 407 (1929).

[19] P. M. Harris, E. Mack and F. C. Blake, THIS JOURNAL, **50**, 1583 (1928).

cules cm.$^{-2}$). The 111 faces contain $\sigma_1 = 4.35 \times 10^{14}$ molecules. It is evident that if one molecule is located above each fluorine ion ($\sigma_1 = 7.75 \times 10^{14}$) the molecules are very much crowded so that repulsive forces (neglected by de Boer) must be of very great importance. These facts invalidate the particular structure assumed by de Boer, in which *atoms* are considered to be arranged in vertical columns over the fluorine ions. Although the molecules in the first layer are probably attached to the fluorine ions, those in the next few layers are thus probably arranged as irregularly as those of liquids, with a tendency to assume a more stable crystalline form at greater distances from the disturbing CaF_2 surface. In any case, however, the exponential decrease in polarization as the number of layers increases should be approximately true, except in the case of the first and second layers.

If we take $\sigma_1 = 5.75 \times 10^{14}$ as the most probable value (after the first layer), we find from the expression for K_1 in Eq. (52)

$$K_1 = 0.57$$

If $\sigma_1 = 4.56 \times 10^{14}$ as given by Eq. (20), the value of K_1 would be 0.64.

In calculating the coefficient 4.3×10^{-16} in Eq. (50) de Boer assumed that the surface of the CaF_2 film was the same as that of the glass on which it was deposited. If the actual surface was 50% larger, this would decrease K_1 from 0.57 to 0.43.

Roughly speaking, therefore, the polarization of any layer of molecules is about one-half of that in the next lower layer. Langmuir,[20] by a study of the dissociation constants of the chlorine-substituted fatty acids, found that the polarizing forces along an aliphatic hydrocarbon chain deformed near one end decrease in the ratio 2.1:1 (or $K_1 = 0.37$) for each successive carbon atom.

Comparing Eqs. (51) and (6) and using the values $K_1 = 0.5$, $K_2 = -6.2$, $K_3 = 1.1$, and $T = 293$ we see that

$$b_n = b_s - 29 + 1800\,(0.5)^n \qquad (53)$$

where b_s is the value of b_0 for solid I_2, which is 7570 according to the data of I. C. T. The term -29 is the contribution of the factor K_3. The disturbance in the regular arrangement of molecules which results from the underlying CaF_2 film raises the limiting vapor pressure for thick layers by 10% ($K_3 = 1.1$), but this is equivalent to a change of b of only 29 out of 7570 or only 0.4%. When we consider that the difference between the liquid and solid state alters b_0 from 5370 to 7570 (see Table I), we realize how insignificant these disturbances are, and how little we should be justified in assuming a value for σ_1 which is appreciably different from that characteristic of solid iodine.

The term $1800(0.5)^n$ in Eq. (53) results from the polarization transmitted from layer to layer. Thus the polarization of the second layer

[20] See reference (15), particularly p. 467.

increases the value by 450 which is only 6% of the value of b_0 for solid iodine.

The exponential factor $(0.5)^n$ is certainly not applicable to the first layer of molecules for these are exposed directly to the powerful polarizing forces of the ions with which they are in contact. We have already seen that glass surfaces (far less effective than CaF_2) raise the value of b_0 for the first layer of nitrogen molecules 2.4-fold, although the polarizability α of N_2 is small compared to that of I_2. If a similar factor can be applied to iodine, the value of b_0 for the first layer on CaF_2 would be about 13,000; compared to this, the effect of the polarization in the second layer is almost wholly negligible.

When, however, the vapor in contact with an adsorbed film is nearly saturated, even these weak polarizing forces naturally produce marked effects. Substituting the values of K_1, K_2 and K_3 in Eq. (51), we calculate that the values of p/p_0 for the successive layers are (for $n > 2$).

n	p/p_0	n	p/p_0
1.01	0.0005	2.0	0.235
1.1	.006	3	.504
1.2	.014	4	.744
1.4	.038	5	.906
1.6	.082	6	1.00

For values of n less than 2, where the exponential relation cannot hold, we have assumed a linear relation between b and n. In the exponent of Eq. (51), $-6.2(0.5)^n$ has been replaced by $1.55(3 - n)$, which gives the same value (1.55) for $n = 2$ and gives a value twice as great as this for the evaporation of isolated molecules from the second layer.[21] The values of p/p_0 obtained by Eq. (51), in the range below $n = 2$, were then multiplied by $\Theta_2 = n - 1$ in accordance with the occurrence of the factor Θ in Eq. (44).

Over the range of pressures p/p_0 from 0.1 to 0.95 covered by de Boer's experiments, n varied only from 1.6 to 5.5. At pressures less than 0.01 p_0 the second layer of molecules rapidly disappears, and the film becomes monomolecular. If b_0 has any such value as 13,000, this monomolecular film would be stable in presence of an iodine pressure as low as 10^{-8} p_0; the average life τ of the molecules in the first layer would be 2000 sec., while that of isolated molecules in the second layer ($b' = 8440$) would be only 4×10^{-4} seconds.

These conclusions, while only approximate, help us to form a clear conception of the relative magnitudes of the factors determining the character of typical adsorbed films. The reasons for the nearly universal

[21] A similar assumption has been found to be approximately true for cesium films on tungsten and is in accord with de Boer's calculation that the mutual repulsion of the dipoles in a complete layer decreases the heat of evaporation (due to dipoles) to one-half of that for single dipoles; see *Proc. Amsterdam Acad.*, **31**, 909 (1928).

monomolecular character of adsorbed films become apparent, but at the same time we are led to understand that under rather special conditions multimolecular layers may form.

Case II, $b' > b_0$.—Liquid mercury (or cadmium) does not wet a glass surface. We may infer that the forces between mercury atoms in liquid mercury are greater than those between a glass surface and mercury atoms in contact with it. Thus the heat of evaporation (kb_0) of adsorbed mercury atoms on glass is less than the heat of evaporation (kb') of atoms from a second or third layer of mercury atoms on glass.

It has been proved experimentally[22] that isolated cadmium atoms evaporate from a glass surface at room temperature enormously more rapidly than do atoms in contact with other cadmium atoms. When cadmium vapor at low pressure strikes a glass surface at $-40°$, nearly all the atoms reëvaporate before they come in contact with other cadmium atoms. If, however, small groups of atoms are formed by raising the pressure of the vapor or by further lowering of the temperature, then these serve as nuclei for the formation of crystals from which there is no appreciable evaporation at room temperature.

Under such conditions the only uniform adsorbed films that can occur are those that cover an extremely small fraction of the surface ($\theta \ll 1$); with higher surface concentrations nuclei are formed and the condensed film is discontinuous. Strong lateral attractive forces between adatoms may also cause these colloidal or granular condensed films to form.

The cases where $b' > b_0$ are to be found particularly where the adsorbate is a substance having a large heat of evaporation (low vapor pressure) and is the type of substance that would be difficultly soluble or miscible with the substance of the adsorbent. Thus since molten metals are not generally miscible with non-metallic liquids, we understand the behavior of mercury and cadmium toward glass.

Such effects may be greatly enhanced by covering the surface of the adsorbent with a monomolecular oil film such as that of a fatty acid. For example, glass surfaces in contact with saturated cesium vapor show marked electrical conductivity because of adsorbed cesium; but a monomolecular oil film on the glass tends to cause the cesium to condense in separated particles and eliminates the conductivity. The hydrocarbon surface is covered with chemically saturated hydrogen atoms from which cesium atoms evaporate far more readily than from cesium metal. A similar phenomenon is responsible for the injurious effect of traces of oily substances on the operation of mercury condensation pumps.

In our present study of evaporation and condensation of adsorbed films, we shall confine ourselves to cases where $b' < b_0$.

Forces Acting between Adatoms.—From measurements of the rate of

[22] Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 141–147 (1917).

evaporation of cesium adatoms on oxygen-covered tungsten, Becker[23] has concluded that the heat of evaporation decreases as θ increases, and from kinetic theory considerations deduces an equation similar to Eq. (40) in which b is a linear function of θ.

Dr. John Bradshaw Taylor has recently[24] completed an extensive series of accurate measurements of the rates of evaporation of atoms (ν_a), of ions (ν_p) and electrons (ν_e) as functions of T from surfaces of pure tungsten on which are adsorbed known numbers (σ) of cesium atoms per unit area. These data afford an opportunity of studying in detail the electrical properties of adsorbed films and the forces acting between adatoms.

The values of ν/θ at 800°K. were found to increase about 10^{10}-fold as θ increases from 0 to 1, indicating very strong repulsive forces between adatoms. The following analysis enables us to determine these forces quantitatively.

Equation of State of Adsorbed Films.—The Gibbs equation for the adsorption isotherm is readily expressed[25] in the form

$$\frac{\mathrm{d}\, F}{\mathrm{d} \ln \mu_a} = \sigma kT \tag{54}$$

where μ_a is given by Eq. (1) and F is the spreading force of the adsorbed film (dynes cm.$^{-1}$). This equation is thermodynamically rigorous if the ideal gas laws apply in the gaseous phase, the surface is homogeneous and is in equilibrium with the vapor. Variations in surface mobility of the adatoms cannot affect the value of F if equilibrium prevails, but they may determine the time of relaxation, *i. e.*, the time required for restoration of equilibrium after a disturbance.

If ν_a can be expressed as a function of θ, then by Eqs. (43) and (54) the spreading force is

$$F = kT \int \sigma \, \mathrm{d} \ln (\nu_a/\alpha) \tag{55}$$

The effect of forces acting between molecules on the equation of state of gases can be calculated by the virial equation[26]

$$pV = RT + \frac{1}{3} \Sigma (rf)$$

where f is the repulsive force that acts between two molecules when their distance apart is r; the summation is to be extended over all pairs of molecules in a gram molecule of gas. In the van der Waals equation

[23] J. A. Becker, *Trans. Am. Electrochem. Soc.*, **55**, 153–173 (1929).

[24] A brief preliminary description of the method used in obtaining these data and of the conclusions drawn from them has been published: Langmuir, THIS JOURNAL, **54**, 1252 (1932). The derivation of the equations there given is contained in the present paper.

[25] See Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 250; Langmuir and Kingdon, *Proc. Roy. Soc.* (London), [A] **107**, 72 (1925).

[26] See Jeans, "Dynamical Theory of Gases," University Press, Cambridge, England.

$$(p + a/V^2)(V - b) = RT$$

the presence of the factor $V - b$ can be deduced by considering the virial of short range repulsive forces which act when molecules come into contact. The term a/V^2 corresponds to the attractive forces of relatively long range.

In an entirely analogous manner the virial may be used to calculate an equation of state for adatoms. In this case

$$FA = RT + \frac{1}{2}\Sigma(rf) \tag{56}$$

where A is the area which contains a gram atom and the summation extends over all the pairs of adatoms in area A.

The two-dimensional van der Waals equation, considering that the long range forces are now repulsive instead of attractive, takes the form

$$(F - a/A^2)(A - A_1) = RT \tag{57}$$

The ordinary derivation of this equation considers only first-order effects as the surface concentration increases; the value of A_1 is then found to be *one-half* the area actually covered by a gram atom of adatoms. Langmuir[27] has tested this equation with experimental data of N. K. Adam on oil films at high surface concentrations and finds that A_1 corresponds to a close packed film in which the molecules unquestionably completely cover the surface. Dr. Lewi Tonks has made a theoretical analysis for the case of adatoms at high concentrations and finds in fact that the value of A_1 should then correspond to the actual area covered instead of one-half that area.

In carrying out the summation in Eq. (56), we may select arbitrarily any atom P as typical and form the sum $\Sigma_1(rf)$ for all the pairs which include the atom P. Since f must decrease very rapidly as r increases, this sum $\Sigma_1(rf)$ is independent of the area over which the summation extends as long as it greatly exceeds molecular dimensions. To form the summation indicated in Eq. (56) we must thus select each atom in turn as a P-atom, finding

$$\Sigma(rf) = (1/2)\sigma A\Sigma_1(rf)$$

where the factor $1/2$ has been introduced in order that we shall not count each pair twice. Substituting this value in Eq. (56) and noting that $A\sigma = R/k$ we obtain

$$F = \sigma kT + (1/4)\sigma\Sigma_1(rf) \tag{58}$$

In order to bring out the relationship between Eqs. (58) and (57) we may rewrite the latter in the form

$$F = \sigma kT/(1 - \sigma/\sigma_1) + a'\sigma^2 \tag{59}$$

and this may be further modified to

$$F = \sigma kT + \sigma^2 kT/(\sigma_1 - \sigma) + a'\sigma^2 \tag{60}$$

By considering the origins of the terms in Eq. (60) and comparing these with the corresponding terms in Eq. (58), we see that the virial term in the

[27] Langmuir, "Third Colloid Symposium Monograph," 1925, p. 72.

latter can be split into two parts: one, $\sigma^2 kT/(\sigma_1 - \sigma)$, corresponds to the short-range forces acting when atoms are in contact, and the other, $a'\sigma^2$, to the long-range repulsive forces. The actual form of the $a'\sigma^2$ term has, however, been based on approximations which will not be sufficiently good for our needs and therefore we may write in place of Eq. (59)

$$F = \sigma_1 kT\Theta/(1 - \Theta) + F' \tag{61}$$

where

$$F' = 0.25\ \sigma\Sigma_1(rf_2) \tag{62}$$

f_2 being the *long range* repulsive force at distance r.

Ordinarily in gas theory the force function $f(r)$ is not definitely known and it falls off with such a high power of the distance that structural properties of the molecules cannot be neglected. Therefore the virial method has not been particularly successful in gas theory. In the theory of electrolytics, however, where the forces decrease less rapidly, the virial proves very useful.[28]

The attractive forces holding adsorbed molecules on surfaces are ordinarily far stronger than those acting among the adsorbed molecules and thus the adsorbed molecules will usually be highly polarized so that they become dipoles having parallel orientations. In general, therefore, we should expect repulsive forces rather than attractive forces to be active between the adsorbed molecules.

In the case of cesium films we have very direct proof that the adatoms act as dipoles. Adsorption of alkali metal atoms occurs strongly only when the electron affinity of the adsorbent metal exceeds the ionizing potential of the alkali, so the act of adsorption probably involves a transfer of the valence electron to the underlying metal. The force holding the atom may thus be regarded as the attraction of the cesium ion and the negative charge induced in the metallic surface (image force). The positive charge on the adatoms manifests itself by changing the contact potential (by as much as 3.0 volts[29] and by a corresponding increase in the electron emission.

The measurements of Langmuir and Kingdon[30] have shown that for a given temperature the electron emission has a maximum at a particular value of Θ. With the surface in this condition the emission is given by $I = AT^2\epsilon^{-b/T}$ with $A = 3.26$ amp. cm.$^{-2}$ deg.$^{-2}$ and $b = 15{,}820$, whereas for a pure tungsten surface the constants are $A = 120$, $b = 53{,}650$. A comparison of these data gives for the contact potential of the optimum cesium surface against pure tungsten $3.26 - 0.31\ (T/1000)$ volts or 3.01 volts at 800°K.

[28] See Milner, *Phil. Mag.*, **25**, 742 (1913), and A. A. Noyes, THIS JOURNAL, **46**, 1080 (1924).

[29] Langmuir and Kingdon, *Phys. Rev.*, **34**, 129 (1929).

[30] Langmuir and Kingdon, *Proc. Roy. Soc.*, (London), **A107**, 61 (1925).

Taylor's experiments have shown that at low temperatures and high cesium pressures, the surface concentration approaches a definite limiting value of 4.8×10^{14} atoms per cm.^{2} of apparent surface (πld) corresponding to $\Theta = 1$. In the preliminary treatment of the filament it was heated for a considerable time to 2800°K. so that appreciable etching by evaporation occurred. Under these conditions the dodecahedral forces (110) are developed.[31] The true surface on which adsorption takes place must therefore exceed the apparent surface. Tonks[32] has shown, on the assumption that the crystal grains have random orientation, that the lowest possible value for the surface excess for dodecahedral faces is 0.225. The number of tungsten atoms per sq. cm. in a dodecahedral face is 1.425×10^{15}.

Simon and Vohsen[33] have found that cesium crystallizes in a body-centered cubic lattice with a lattice constant 6.05 Å. at liquid air temperature (about 6.17 Å. at room temperature). Tungsten has the same type of lattice but the constant is 3.15 Å. Thus if cesium atoms arrange themselves on the face of a dodecahedral tungsten crystal so that there is one cesium atom for every four tungsten atoms, the surface lattice is identical in type and in spacing (within 2%) with that occurring in a similar face of a cesium crystal. Since the strongest forces exerted on the adatoms are those originating from the underlying tungsten atoms, we may therefore, with considerable confidence, take for $\Theta = 1$

$$\sigma_1 = 3.563 \times 10^{14} \text{ atoms cm.}^{-2} \qquad (63)$$

for the true surface density of a complete monatomic cesium film on tungsten. Comparing this with the apparent surface density 4.8×10^{14} we conclude that the ratio of the true to the apparent surface is 1.347 as compared to 1.225 for the *minimum value* of this ratio calculated by Tonks.

Taylor's data show that the optimum electron emission occurs at $\Theta = 0.67$ corresponding to $\sigma = 2.4 \times 10^{14}$.

Simon and Vohsen's data give 5.34 Å. as the shortest distance between the atoms in metallic cesium. A sphere of this diameter, having unit positive charge, in contact with an ideal plane conducting surface, produces an external electric field equivalent to that of a dipole (without neighboring conductor) having a moment $M = 25.4 \times 10^{-18}$.

If a conducting surface is covered with σ such ions per unit area, each having a dipole moment M, the contact potential V_c against a bare surface of the same material would be

$$V_c = 2\pi M\sigma \text{ (c. g. s. u.)} = 1885\, M\sigma \text{ volts} \qquad (64)$$

Placing $\sigma = 2.4 \times 10^{14}$ and $M = 25.4 \times 10^{18}$ we obtain $V_c = 11.6$ volts, which is 3.84 times the 3.01 volts observed for the surface of optimum emission.

[31] Langmuir, *Phys. Rev.*, **22**, 374 (1923).

[32] Tonks, *ibid.*, **38**, 1030 (1931).

[33] Simon and Vohsen, *Z. physik. Chem.*, **133**, 165–187 (1928).

It is evident that the strong field (10^8 volts per cm.) in the double layer draws electrons from the tungsten to a plane which lies only 0.69 Å. below that of the centers of the adatoms. The actual dipole moment per atom in a film of optimum emission is thus only $M = 6.1 \times 10^{-18}$.

Assuming that M is independent of surface concentration Langmuir has calculated[34] that the logarithm of the electron emission of a metal partly covered by adatoms of an electropositive metal should be a linear function of Θ. Becker[23] has determined the electron emission from monatomic barium films on tungsten at 1100°K. The curve of $\log_{10}(i/i_W)$ against Θ gives a maximum at $\Theta = 1$ of 11.3 while the initial slope is 25. We may interpret this as indicating that for low values of Θ, M is 2.2 times as great as for a film giving the optimum emission. Becker implies that the curve for cesium on tungsten is closely similar. If we may thus use the factor 2.2, we conclude that for very dilute cesium films $M = 14.6 \times 10^{-18}$, which is 0.57 of that which we estimated for cesium ions on an idealized plane conductor. The decrease in M as Θ increases is to be attributed to the depolarizing effect of the field produced by the adatoms.

Let us now calculate by the virial method the equation of state of adsorbed cesium atoms. Although the electric field produced by an ion on a conducting surface is the same as that of a dipole (without the presence of the conductor), the force acting between adions is not equal to that between the two dipoles, for we must consider only the force on the real ion and not that on its image. The force acting between two adions separated by the distance r, being half that between dipoles is thus

$$f = (3/2)\, M^2/r^4 \tag{65}$$

and the potential energy in electron volts is

$$Ve = (1/2)M^2/r^3 \text{ or } V = 3.14 \times 10^{11}\, M^2/r^3 \text{ volts} \tag{66}$$

The effect of the repulsive forces between adatoms is to decrease the concentration of other atoms in the neighborhood of a given atom in accord with the Boltzmann equation

$$\sigma = \sigma' \epsilon^{-Ve/kT} \tag{67}$$

where e/k has the value 11,600 degrees per volt. To form an estimate of the magnitude of this effect, let us imagine for simplicity that the elementary spaces which can hold adatoms are arranged in an hexagonal lattice (honeycomb structure). With $\sigma_1 = 3.563 \times 10^{14}$ this gives $r_1 = 5.69$ Å. for the shortest distance between atoms. At this distance for $M = 14.6 \times 10^{-18}$ we find by Eq. (66) that $V = 0.365$ volt and thus by Eq. (67) at $T = 800$ the probability that one of the six available spaces adjacent to a given atom will be occupied is only 0.005 as great as that for the distant spaces. The next ring contains 12 spaces, half of which are at a distance 9.9 Å. and

[34] Langmuir, *Phys. Rev.*, **22**, 364 (1923). A fuller discussion is given by W. Schottky and H. Rothe, "Handbuch Exptl. Physik," XIII, [2] 1928, pp. 160–167.

the other half at 11.8 Å. from the central atom. For these $V = 0.069$ and 0.041 volt and the corresponding probabilities are 0.37 and 0.55.

Since these nearest 18 spaces tend to be far less densely populated than an average space, the distribution of the atoms will be much more uniform than if there were no forces acting and will approximate to a regular lattice arrangement. Let us therefore at first calculate the virial term $\Sigma_1(rf)$ in Eq. (62) on the assumption that the atoms are in an hexagonal lattice,[35] the shortest distance r_1 between them being given by

$$r_1 = (4/3)^{1/4}\sigma^{-1/2} = 5.69 \times 10^{-8}/\Theta^{1/2} \text{ cm.} \tag{68}$$

Using the value of f from Eq. (65) we see that

$$\Sigma_1(rf) = (3/2)M^2\Sigma_1(1/r^3) \tag{69}$$

By adding the values of $1/r^3$ for the separate atoms in an hexagonal surface lattice, using an accurate empirical integration process for the more distant atoms, it was found that

$$\Sigma_1(1/r^3) = 11.044/r_1^3 \tag{70}$$

Combining Eqs. (61), (62), (69), (70) and (68)

$$F = \sigma_1 kT\Theta/(1 - \Theta) + 3.338\,\sigma^{5/2}\,M^2 \tag{71}$$

This gives the equation of state on the assumption that the adatoms are arranged in a plane hexagonal lattice. This should be a fairly good approximation at higher values of Θ. The last term must quite accurately represent the virial contribution of all the adatoms which are at distances as great as r_1. The atoms nearer than this must, however, often contribute materially to the virial. We may take these into account as follows.

At distances much less than r_1 the concentration is determined largely by the potential energy of the adatoms in accord with Eq. (67).

The contribution to $\Sigma_1(1/r^3)$ furnished by the atoms that lie within a circular ring is thus

$$\Sigma_1(1/r^3) = \int_{r_0}^{r_2} 2\pi r\, dr(1/r^3)\sigma_2 \exp.\,(-Ve/kT) \tag{72}$$

where r_2 and r_0 are the outer and inner radii of the ring, σ_2 is the surface concentration of atoms at $r = r_2$ and Ve is the change in potential energy when an atom is moved from r_2 to r.

At distances greater than about r_1, given by Eq. (68), V remains constant because the forces from the separate atoms must on the average balance one another. If we choose a suitable value for r_2, somewhat less than r_1, we may thus put in accord with Eq. (66).

$$Ve/kT = (M^2/2kT)(r^{-3} - r_2^{-3}) \tag{73}$$

For values of r greater than r_2 we may take $V = 0$ and may replace the actual discontinuous distribution of adatoms by an equivalent continuous

[35] It should be noted that this hypothetical lattice is not related to that of the underlying tungsten atoms, but varies continuously in lattice constant as Θ changes. It expresses merely the fact that the repulsive forces are effective in establishing a far more uniform distribution than if the adatoms were in random positions.

distribution. Thus the contribution to $\Sigma_1(1/r^3)$ resulting from adatoms beyond r_2 is

$$\Sigma_1(1/r^3) = \int_{r_2}^{\infty} 2\pi r \, dr(1/r^3)\sigma_2 = 2\pi\sigma_2/r_2 \tag{74}$$

Since we have already found that the contribution of the more distant atoms is given by Eq. (70), we may compare these two expressions to determine the appropriate value of r_2. Since σ_2 may be identified with σ, we thus find from Eqs. (70), (74) and (68)

$$r_2 = 2\pi\sigma r_1^3/11.044 = (2\pi/11.044)(4/3)^{3/4}\sigma^{-1/2} = 0.7059\sigma^{-1/2} \tag{75}$$

With this value of r_2, we can now derive an improved expression for F by merely adding to Eq. (71) a term

$$F'' = (3/8)\sigma M^2\Sigma_1(1/r^3) \tag{76}$$

in accord with Eqs. (62) and (69), the sum $\Sigma_1(1/r^3)$ being given by Eq. (72). To integrate Eq. (72) we may substitute

$$u^3 = M^2/2kTr^3 \tag{77}$$

and obtain

$$\left.\begin{aligned} F'' &= (3\pi/4)(2kT)^{1/3}M^{4/3}\sigma^2 I \\ \text{or} \quad F'' &= 1.531 \times 10^{-5}\,\sigma^2 T^{1/3}M^{4/3}I \end{aligned}\right\} \tag{78}$$

where the integral I is

$$I = \exp.(u_2^3)\int_{u_2}^{u_0} d\,x \exp.(-x^3) \tag{79}$$

The values of u_2 and u_0 are found by Eq. (77) from the corresponding values of r_2 and r_0. The former is given by Eq. (75), while r_0 may be obtained from this same equation by replacing σ by σ_1. Thus, after introducing the numerical value of k, we have

$$\left.\begin{aligned} u_0 &= 2.181 \times 10^5\, M^{2/3}\, T^{-1/3}\,(\sigma_1)^{1/2} \\ \text{and} \quad u_2 &= 2.181 \times 10^5\, M^{2/3}T^{-1/3}\,(\sigma_1)^{1/2}\Theta^{1/2} \end{aligned}\right\} \tag{80}$$

The spreading force F' due to the long range forces between adatoms, as defined by Eq. (62), can be obtained by adding F'' from Eq. (78) to the last term of Eq. (71) giving

$$F' = 3.338\,\sigma^{5/2}M^2 + 1.531 \times 10^{-5}\,\sigma^2 T^{1/3}M^{4/3}I \tag{81}$$

The complete equation of state of the adsorbed film is then given by Eq. (61) after inserting this expression for F'.

Calculation of F′ from Experimental Data on ν_a.—Differentiation of Eq. (61) gives

$$d\,F = \sigma_1 kT d\Theta/(1-\Theta)^2 + d\,F' \tag{82}$$

Taylor's experiments have shown that for cesium films $\alpha = 1$ and therefore by Eq. (43) we may identify ν_a with μ_a. Thus integration of Eq. (54) gives

$$\ln \nu_a = \frac{1}{\sigma_1 kT}\int \frac{dF}{\Theta} \tag{83}$$

Introducing the value of d F from Eq. (82) and integrating

$$\ln \nu_a = \ln [\theta/(1 - \theta)] + 1/(1 - \theta) + (1/\sigma_1 kT) \int d F'/\theta \quad (84)$$

Taylor's experimental data on ν_a can be expressed in the form

$$\ln [\nu_a(1 - \theta)/\theta] - 1/(1 - \theta) = A - B/T \quad (85)$$

where A and B are functions of θ only. The data give

$$A = 61.0 + 4.8\,\theta - 2.4\,\theta^2 \quad (86)$$

For values of θ up to 0.6 the values of B can be represented within the experimental error (about 0.3%) by the empirical equation

$$B = 32{,}380/(1 + 0.714\,\theta) \quad (87)$$

Beyond $\theta = 0.6$ the experimental values of B gradually become somewhat larger than those given by Eq. (87), but this deviation is only 2% at $\theta = 0.8$ and 4% at $\theta = 0.9$.

By eliminating ν_a from Eqs. (84) and (85) we obtain

$$\int (1/\theta) dF' = \sigma_1 kT(A - B/T) \quad (88)$$

Differentiation with respect to θ and multiplication by θ gives

$$\frac{dF'}{d\theta} = \sigma_1 k\theta \left(T \frac{dA}{d\theta} - \frac{dB}{d\theta}\right) \quad (89)$$

By integration we obtain an expression for F'

$$F' = \sigma_1 k \left[T \int \theta(dA/d\theta)d\theta - \int \theta\,(dB/d\theta)d\theta\right] \quad (90)$$

Inserting the values of A and B from Eqs. (86) and (87) and placing $\sigma_1 k = 0.04884$ in accord with Eq. (63), we get from Taylor's data

$$F' = (0.1172\,\theta^2 - 0.078\,\theta^3)\,T + 2215\,[\ln(1 + \beta\theta) - \beta\theta/(1 + \beta\theta)] \quad (91)$$

where $\beta = 0.714$, the coefficient in the denominator in Eq. (87). The integration constant was so chosen as to make $F' = 0$ at $\theta = 0$. This expression gives that part of the spreading force (in dynes cm.$^{-1}$) which is due to the dipole repulsion of the cesium atoms.

Values of F' calculated by Eq. (91) for $T = 800$ are given in the third column of Table III. The second column gives the total spreading force F obtained from F by Eq. (61).

Calculation of Dipole Moment M.—By equating the theoretical and the experimental expressions for F', given by Eqs. (81) and (91), an equation is obtained which may be solved for M. By inserting the value of σ_1 from Eq. (63), Eq. (81) may be written

$$F' = 8.00\,x^3\theta^{5/2} + 1.943\,x^2 T^{1/3}\theta^2 I \quad (92)$$

where

$$x = 10^{12} M^{2/3} \quad (93)$$

The values of F' for any particular values of θ and T are first calculated from Eq. (91) and these are inserted in Eq. (92). These cubic equations in x may be readily solved by Horner's method. A difficulty arises from the fact that the integral I, according to Eqs. (79) and (80), is itself a function

of x. However, by a series of rapidly converging approximations, it is found possible without much labor to evaluate the integral with sufficient accuracy to get x to 3 or 4 significant figures. This procedure is facilitated by the fact that the term in Eq. (81) which contains I is small compared to the other term. (Ratio is 0.4 at $\Theta = 0.1$, 0.18 at $\Theta = 0.3$, 0.09 at $\Theta = 0.7$.)

TABLE III

CESIUM FILMS ON TUNGSTEN[36]

Spreading force F, dipole moment M, contact potential V and depolarizing field E, all calculated from ν_a at $T = 800°K$.

1	2	3	4	5	6	7
Θ	F, dynes cm.$^{-1}$	F',	I	$10^{18} M$ c. g. s. (e. s.)	V, volts	$10^{-6} E$ volt cm.$^{-1}$
0.0	0	0	0.893	16.16	0	0
.1	10.35	6.01	.315	13.01	0.874	10.4
.2	31.9	22.1	.237	11.17	1.500	22.2
.3	62.6	45.9	.200	9.94	2.003	34.6
.4	101.4	75.4	.180	9.01	2.420	47.0
.5	148.2	109.1	.163	8.28	2.780	59.2
.6	204.3	145.7	.148	7.67	3.089	71.1
.7	271.9	180.7	.130	7.10	3.328	81.6
.8	366.9	210.6	.102	6.54	3.515	90.4
.9	586.9	235.2	.048	6.06	3.663	96.8

The values of I and M obtained in this way are given in the fourth and fifth columns of Table III. The contact potential V of the cesium covered surface against a pure tungsten surface, as calculated from M by Eq. (64), is given in the sixth column.

Depolarizing Field.—Every adatom on the surface is acted on by the electric field produced by all the neighboring adatoms. A dipole of moment M on a surface, with its axis normal to the surface, produces a field of intensity Mr^{-3} at a point on the surface whose distance from the dipole is r. To obtain the total field E acting on a given adatom we must sum the contributions of all neighboring adatoms

$$E = M\Sigma_1(r^{-3})$$

By eliminating f between Eqs. (62) and (65) we find that

$$F' = (3/8)\sigma M^2\Sigma_1(r^{-3})$$

and therefore

$$E = (8/3\sigma_1)F'/\Theta M = 2.245 \times 10^{-12}\, F'/\Theta M \text{ volts cm.}^{-1} \qquad (94)$$

The last column in Table III contains values of E (in millions of volts cm.$^{-1}$) calculated by this equation. The magnitude of these fields seems adequate to cause the marked decrease in M that occurs as Θ increases.

Electron Emission ν_e.—Consider a plane tungsten surface part of which is bare while the rest is covered by an adsorbed film of cesium con-

[36] The values of Θ in the 1st column refer to the cesium on the homogeneous part of the surface (see later section). These were obtained from the observed values $\Theta_{obs.}$ by the equation $\Theta = \Theta_{obs.} - 0.005$.

taining σ atoms cm.$^{-2}$. Under equilibrium conditions at temperature T the concentration of electrons over the surface is governed by the Boltzmann equation and therefore if there is no appreciable reflection of low velocity electrons from the surface we have

$$\nu_e/\nu_w = \exp.\,(Ve/kT) \tag{95}$$

where ν_e and ν_w are, respectively, the rates of evaporation of electrons from the cesium covered and from the bare tungsten surfaces, V being the contact difference of potential between these surfaces.

The electron emission from pure tungsten according to Dushman is given by

$$I = 60.2\ T^2\ \epsilon^{-b/T}\ \text{amp. cm.}^{-2}$$

where $b = 52{,}400$ was obtained by experiments in the range of temperatures from 1400 to 2400°K. The coefficient 60.2 was calculated by the Sackur–Tetrode relation. At the time of Dushman's derivation the electron-spin was not known to exist. If this is taken into account[37] the coefficient should be 120.4. This change of coefficient requires a change of b from 52,400 to 53,650 if the values of I and of dI/dT are to keep their same values at $T = 1800$°K. At 1400 and at 2400° the values of I obtained by the new equation differ by less than 20% from those given by the original equation, although over this range of temperature the emission increases 2×10^7-fold. These differences are probably within the experimental error. Since our present interest lies in the range of temperature down to 600°, where the difference between the two equations amounts to a factor of about 4, it seems better to adopt the equation which is in accord with modern theory.

The revised equation can be expressed

$$\nu_w = 4\pi m\,(kT)^2h^{-3}\exp.\,(-V_we/kT) \tag{96}$$

where $V_we/k = 53{,}650$ and V_w, the electron affinity of pure tungsten, has the value

$$V_w = 4.622\ \text{volts} \tag{97}$$

Within the range from 600 to 1000° the values of ν_w from Eq. (96) are very closely given by

$$\ln \nu_w = 63.44 - 55{,}250/T \tag{98}$$

Combining this with Eq. (95) we get

$$\ln \nu_e = 63.44 - e/kT(4.760 - V) \tag{99}$$

By inserting the values of V from Table III for any particular value of Θ (and T), the electron emission ν_e can be calculated from data on ν_a. Since these values are derived on the assumption of equilibrium, they correspond to the electron emission at zero accelerating field.

Positive Ion Emission ν_p.—In an enclosure containing cesium vapor,

[37] See Fowler's "Statistical Mechanics," University Press, Cambridge, England.

under conditions of equilibrium, the law of mass action requires that the concentrations n_e, n_p and n_a of electrons, ions and atoms fulfil the condition

$$K_n = n_e n_p / n_a \tag{100}$$

Using the third law of thermodynamics, the equilibrium constant K_n is found[38] to be

$$K_n = \frac{\omega_e \omega_p}{\omega_a} \frac{(2\pi m_e kT)^{3/2}}{h^3} \exp.\ (-V_i e/kT) \tag{101}$$

where V_i, the ionizing potential, is

$$V_i = 3.874 \text{ volts}$$

for cesium. The statistical weights ω have the values $\omega_e = \omega_a = 2$ and $\omega_p = 1$. The concentrations n are related to the corresponding ν according to the kinetic theory by

$$\nu = n(kT/2\pi m)^{1/2} \tag{102}$$

We may thus place

$$K_\nu = \nu_e \nu_p / \nu_a = 2\pi m (kT)^2 h^{-3} \exp.\ (-V_i e/kT) \tag{103}$$

Combining this equation with Eqs. (96) and (95) we get

$$\ln (2\nu_p) = \ln \nu_a + (e/kT)(V_w - V_i - V) \tag{104}$$

Using the values of V in Table III we see that the rate of ion evaporation ν_p (for zero accelerating field) can be calculated wholly from atom evaporation data.

Comparison with Experiment.—The values of M and V in Table III have been calculated from the data on ν_a given by Eq. (85) taking $T = 800°$. The values obtained by similar calculations using $T = 600$ or $T = 1000$ are practically identical with those at 800° (within about 0.02 volt for V). This shows that the temperature coefficient of F' is adequately represented by the last term in Eq. (92) which originates from the changing distribution of the adatoms in accord with the Boltzmann equation. At low temperatures the distribution is governed mainly by the repulsive forces which tend to bring about a regular lattice arrangement, but at high temperatures thermal movements cause some of the atoms to approach closer to one another than corresponds to this lattice. We see by Eq. (90) that the temperature coefficient of F' is associated with a dependence of A on Θ.

The value of A from the experiments, as given by Eq. (86), is of the same order of magnitude as that given by Eq. (41) which we obtained from our general vapor pressure equations. Thus inserting $T = 800$ and $M = 133$ in Eq. (41) and comparing with Eq. (85) (neglecting the terms containing $1 - \Theta$) we find $A = 65.8$ in place of the values given by Eq. (86). This equation gives $A = 65.8$ at $\Theta = 0.66$.

In our derivation of Eqs. (40) and (41) b was assumed to be independent

[38] Fowler, "Statistical Mechanics," 1929, p. 281.

of temperature. The variation of the adatom distribution with temperature, due to the Boltzmann effect, must cause slight changes in the heat of evaporation, at constant Θ, and corresponding changes in b. This is indistinguishable in its effect from a dependence of A upon Θ and therefore in the present case with strong forces between the adatoms we should not expect A to be strictly constant.

In his experiments Taylor has determined ν_e and ν_p as functions of T, Θ and the accelerating field. At high fields, such as are obtained with 40 to 200 volts on the cylinder (field of 3000 to 15,000 volts cm.$^{-1}$ at filament), the variation is approximately in accord with Schottky's theory, but at lower fields the variation is far greater than given by this theory.[39] By plotting the logarithms of ν_e or ν_p against the cylinder potential, a rapid change of slope (kink) occurs as the field changes from retarding to accelerating. The values of ν_e at this kink are about one-half to one-seventh of those obtained with accelerating fields of 3000 volts cm.$^{-1}$. These are presumably the values that correspond to the thermodynamic equilibrium implied in Eqs. (99) and (104). As a matter of fact, the experimentally determined values of ν_e and ν_p at the kink agree very satisfactorily with those calculated by these equations (from data on ν_a) up to values of $\Theta = 0.5$. The observed values of ν_e for $\Theta > 0.5$ fall below those calculated. A full report of Taylor's experiments, soon to be published, will contain a more detailed comparison of the experimental and theoretical results.

The agreement obtained seems sufficient to justify the belief that the foregoing analysis of the effects of dipole forces between adatoms on plane surfaces is substantially correct, except for very concentrated films.

General Characteristics of Atom Evaporation from Cesium Films.—The observed variation of ν with Θ as expressed in Eqs. (85), (86) and (87) is very different from that of the adsorption isotherm of Eq. (2). The occurrence of Θ in the denominator of the B term in Eq. (85) causes an increase of ν with Θ of the exponential type.

This characteristic of the evaporation is illustrated in another way in Fig. 1 which shows the rate of decrease in Θ by evaporation when a filament is maintained at constant temperature in a space free from cesium vapor (bulb in liquid air). Within any narrow range in values of Θ the rate of evaporation ν_a is approximately proportional to an exponential function of Θ so that we can put

$$\nu_a = Ke^{H\Theta}$$

where H varies only slowly with Θ. To construct a given curve, for example that for 700°, having a time scale covering one-half hour, we are interested only in values of ν_a from 10^{10} to 10^{12} which occur for values of Θ between 0.23 and 0.40. In this range H varies only from 34 to 30.

[39] K. T. Compton and I. Langmuir, *Rev. Modern Phys.*, **2**, 123–242 (1930); see especially pp. 146–157.

Since $\sigma_1(d\theta/dt) = \nu_a$, we can calculate the time interval required to pass from Θ_2 to Θ_1 by integration, treating H as constant in this range; thus

$$t = \frac{\sigma_1}{H}\left(\frac{1}{\nu_1} - \frac{1}{\nu_2}\right) \tag{105}$$

where ν_1 and ν_2 are the values of ν_a corresponding to Θ_1 and Θ_2. The four full-line curves in Fig. 1 have been prepared in this way.

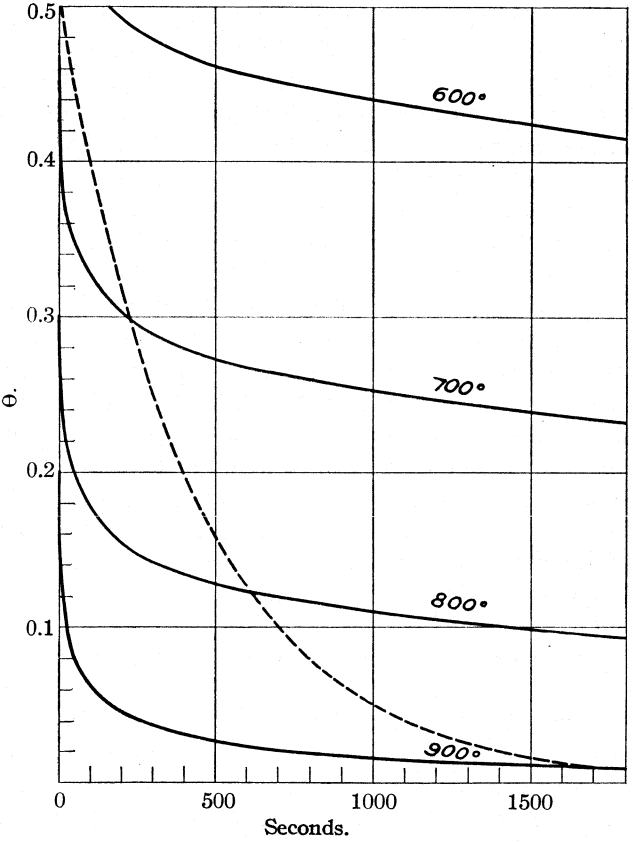


Fig. 1.—Evaporation of cerium films from tungsten at various temperatures. The dotted line is an exponential curve.

The dotted line curve gives for comparison an ordinary exponential curve $y = b\epsilon^{-ax}$, which corresponds to evaporation on the assumption that the rate is proportional to Θ, *i. e.*, that there are no repulsive forces between adatoms. A striking feature of the evaporation from cesium films on tungsten is the fact that Θ decreases almost instantly from $\Theta = 1$ down to a certain value and then tends to approach a limiting value. Thus at 700°, Θ falls to 0.4 in 10 sec., to 0.25 in 1080 sec., but would take 10.5 hours to fall

to 0.15 and 80 hours to reach 0.1. Similar effects are observable with oxygen films on tungsten and point to the presence of strong repulsive forces between adatoms.

Homogeneity of the Tungsten Surface.—In this paper we have so far tacitly assumed that the tungsten surface is homogeneous in the sense that the life τ of any adatom is independent of its position on the surface. The variation of τ with Θ has been taken to be evidence of forces between adatoms.

In the author's 1918 paper on adsorption[40] the second and third typical cases that were considered were based on the assumed presence of more than one kind of elementary space. The surface may be considered as divided into infinitesimal fractions $d\beta$, each element having its own characteristic evaporation rate ν_1 if saturated with adatoms. Thus ν_1 expressed as a function of β gives a "law of distribution" of the evaporation rate ν_1 over the surface. If there are no forces acting between adatoms, Eq. (2) can be applied to each element $d\beta$ and thus by integration it was found for the whole surface that

$$\sigma = \sigma_1\Theta = \int_0^1 (\nu_1 + \alpha_0\mu)^{-1}\,\alpha_0\mu d\beta \qquad (106)$$

The practical importance of *active areas* in determining the catalytic properties of surfaces (even plane surfaces) was pointed out in a later paper.[41] Within recent years many experimental and theoretical studies have been made of active spots, especially by H. S. Taylor and his collaborators.

It is evident from Eq. (106) that by assuming a heterogeneous tungsten surface, that is, by properly choosing the function $\nu_1(\beta)$, any observed law of variation of ν_a with Θ, such as that expressed by Eqs. (85), (86) and (87), can be accounted for without the necessity of postulating forces between adatoms. However, in this case M would be zero and thus the electron emission ν_e would not vary with Θ. The fact that the observed values of ν_e and ν_p agree with those calculated by Eqs. (99) and (104) from the values of M in Eq. (81) proves conclusively that the tungsten surface is essentially homogeneous.

Active Spots on Tungsten Surface.—The foregoing conclusion is justified by Taylor's experimental data on ν_a for values of Θ greater than about 0.05. In our first detailed analysis of the data obtained with still more dilute cesium films, it was found that the observed values of ν_a were considerably less than those calculated by Eqs. (85), (86) and (87). Since the equation of state of the two-dimensional gas film should approach more nearly to the ideal gas law $F = \sigma kT$ at low concentrations, it appeared to

[40] Langmuir, THIS JOURNAL, **40**, 1361 (1918), see particularly p. 1371.

[41] Langmuir, *Trans. Faraday Soc.*, **17**, 607 (1921), see especially pp. 617 and 618. This paper was reprinted in *Gen. Elec. Rev.*, **25**, 445 (1922).

be impossible to account for these deviations on assumption that the tungsten surface was wholly homogeneous.

It was found that this difficulty disappeared entirely if it was assumed that about 0.50% of the tungsten surface holds cesium so much more firmly than the rest, that this *active surface* becomes saturated before more than 0.5% of the remaining surface is occupied. The total surface concentration may thus be divided into two parts

$$\sigma = \sigma_a + \sigma_n = \sigma_1(\Theta_a + \Theta_n) \tag{107}$$

where the subscripts refer to the *active* and to the *normal* parts of the surface. Evidently when the active surface becomes saturated, so that $\Theta_a = 0.005$, we may put

$$\Theta_n = \Theta_{obs.} - 0.005 \tag{108}$$

If ν_a is calculated by Eqs. (85), (86) and (87), using Θ_n instead of $\Theta_{obs.}$, the values are found to agree with those found by Taylor's experiments down to values of $\Theta_{obs.}$ as low as 0.01. The reason for the discrepancies that remain at still lower values of Θ are then explainable as due to a lack of complete saturation on the active surface. In this way, by Eq. (107), subtracting the calculated values of Θ_n from $\Theta_{obs.}$, we can obtain Θ_a from experiments carried out with known values of T and μ. In an analysis of Taylor's data (to be published) it will be shown that

$$\ln [\mu(0.005 - \Theta_a)/\Theta_a] = 65.8 - 44{,}440/T \tag{109}$$

expresses quite accurately the variation of Θ_a with T and μ.

The degree of saturation of the active surface, $\Theta' = \Theta_a/0.005$, thus approaches unity as μ increases or T decreases. Comparison of Eq. (109) with Eqs. (85), (86) and (87) shows that B is independent of Θ'. The experiments show strikingly that the evaporation from the active surface resembles that illustrated by the dotted curve in Fig. 1 instead of the full line curves. A moderate increase of temperature causes practically all of the adatoms to evaporate from the active surface.

This constancy of B proves that repulsive forces do not act between the adatoms on the active surface. This must mean that the active areas consist of isolated elementary spaces, each capable of holding one adatom. It is probable that these active spots are located at points where the spacing of the tungsten atoms is abnormal and is particularly favorable for holding cesium atoms. Such positions may occur close to grain boundaries where the tungsten lattice must be disturbed. The filaments in Taylor's experiments had a very fine-grained crystalline structure which had been considerably etched by heating to 2800°K.

It is probable that the extent of the active area can be made to vary by heat treatment of the filament, but that the properties of the normal part of the surface are uninfluenced by such treatment.

If we solve Eq. (2) for ν_1 we find

$$\nu_1 = \mu(1 - \Theta)/\Theta \tag{110}$$

Since the rate of evaporation ν_1 for a saturated surface varies with temperature in such a way that $\ln \nu_1$ is a linear function of $1/T$, we thus see that Eq. (109) is of a form that is directly derivable from Eq. (2).

It seems probable that the cases in which Eq. (2) is applicable to adsorption on plane surfaces are those in which the elementary spaces available for adsorption are isolated from one another. Only in such cases does it seem reasonable that the average life of adatoms shall be independent of θ and that the rate of condensation shall be proportional to $\theta_s - \theta$, where θ_s corresponds to saturation of these spaces. In general, therefore, when Eq. (2) applies we should expect θ_s to be considerably less than unity. This was observed in the case of adsorption of gases on glass and mica.[1]

Effect of Oxygen.—The foregoing theories of the nature of cesium films on tungsten aid in understanding the effects observed when the tungsten is partly covered by adsorbed oxygen before bringing into contact with cesium vapor. The oxygen decreases the rate of evaporation of cesium atoms so greatly that the filament can be heated about 250° higher before losing its cesium film. This is now explainable as the result of attractive forces between the negative dipoles of the oxygen adatoms and the positive cesium dipoles. The cesium atoms thus form clusters about every oxygen adatom and will also cover the oxygen atoms. The effect of the oxygen will also be to increase the dipole moment of the cesium adatoms. The presence of minute amounts of oxygen should manifest itself by producing active spots which can be investigated by the methods outlined above.

It is our plan to investigate experimentally these effects of traces of oxygen.

Summary

The vapor pressures of liquids can be expressed (in baryes) by

$$p = AT^{\gamma} \exp.(-b/T)$$

where A, γ and b are constants. Trouton's rule is equivalent to postulating that $\gamma = 0$ and A = a universal constant. Vapor pressure data of "International Critical Tables" give $\log A = 10.65$ with a standard deviation (S. D.) of 1.19. Hildebrand's rule is equivalent to taking $\gamma = 1$ and A is then a universal constant for which $\log A = 7.83$ with S. D. = 0.52. A rule which agrees still better with the data is obtained by putting $\gamma = 1.5$ and then it is found that $\log A_{1.5} = 6.37$ with a S. D. = 0.22, which is less than half as great as that for Hildebrand's rule.

The vapor pressures of solids whose vapors have rigid molecules are also given by this equation with $\gamma = 1.5$ and $\log A = 6.9$. Much larger values of A are obtained for solids if the molecules possess internal degrees of freedom. The concept is advanced that such molecules in the vapor phase at higher temperatures may possess high internal mobility (as though

liquid) while at lower temperatures they may become rigid (as though solid). Such effects probably do not exist with molecules of vapors of liquids.

These vapor pressure equations may be applied to adsorption phenomena. The rate of evaporation of atoms or molecules from monatomic films on surfaces is thus given by

$$\nu = A_{1.5}(2\pi mk)^{-1/2}\,\Theta T \exp.\,(-b/T)$$

This is found to agree reasonably well with experimental data on thorium, oxygen and cesium films on tungsten.

The conditions are discussed which lead to the formation of monatomic and of polyatomic adsorbed films. It is emphasized that the latter can occur on plane surfaces only under rather unusual conditions.

In general adsorbed molecules on plane homogeneous surfaces are acted upon by strong forces originating from the underlying solid. The resulting polarization causes the adsorbed molecules to repel one another as dipoles, with forces varying in proportion to M^2r^{-4} where M is the dipole moment and r the distance. Attractive forces predominate only if two kinds of adsorbed molecules are present which become polarized in opposite senses, as for example cesium and oxygen on tungsten (or salt-like substances on metals, such as mercurous sulfate on mercury).

The equation of state of the two-dimensional gas constituting the adsorbed film is worked out for molecules which repel as dipoles by means of the Clausius virial. By use of Gibbs' equation for the adsorption isotherm the rate of evaporation ν can be worked out in terms of Θ, T and M. The equations are found to be of the form required by experimental data on cesium films on tungsten. Thus the experimental data furnish values of M as a function of Θ.

The Boltzmann equation and the Saha equation then permit the calculation of the rates of evaporation of electrons (ν_e) and of ions (ν_p) from $M(\Theta)$ and T, yielding results in agreement with experiment. The results indicate that the tungsten surface is essentially homogeneous except for about 0.5% of the surface which holds cesium atoms much more firmly than the rest.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE BEHAVIOR OF GERMANIUM TETRACHLORIDE AND RELATED CHLORIDES, ESPECIALLY ARSENIOUS CHLORIDE, WITH CONCENTRATED HYDROCHLORIC ACID[1]

BY ELTON R. ALLISON AND JOHN H. MÜLLER

RECEIVED APRIL 20, 1932 PUBLISHED JULY 6, 1932

Procedures for the separation of germanium from arsenic have followed two general methods: the distillation of germanium tetrachloride from a hydrochloric acid solution of germanium dioxide under conditions which keep arsenic in the pentavalent state of oxidation, and the precipitation of arsenic as sulfide under conditions which prevent the precipitation of germanium sulfide. The method proposed by Dennis and Johnson,[2] using a current of chlorine and a special still head, is the most efficient distillation process. Abrahams and Müller[3] have recently described a method for the sulfide separation which is particularly valuable for analytical purposes.

The purpose of this investigation was to study an extraction method for the removal of arsenious chloride from germanic chloride. Friedrich[4] first noticed that germanium tetrachloride was immiscible with and unaffected by concentrated sulfuric acid. Dennis and Hance[5] observed that concentrated nitric acid attacked germanium tetrachloride, although somewhat slowly. The effect of concentrated hydrochloric acid on germanium tetrachloride has not been studied, while it is known that arsenious chloride has a high solubility in this acid.[6]

Preliminary experiments showed that concentrated sulfuric acid was not suitable for the extraction of arsenious chloride from germanic chloride because of the low solubility of arsenious chloride in the acid. Germanium tetrachloride was found to be practically insoluble in concentrated hydrochloric acid. The distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride was investigated and the extraction of arsenious chloride from germanic chloride by means of concentrated hydrochloric acid studied as a purification method.

[1] This paper is based on a thesis submitted by Elton R. Allison to the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Dennis and Johnson, THIS JOURNAL, **45**, 1380 (1923).

[3] Abrahams and Müller, *ibid.*, **54**, 86 (1932).

[4] Friedrich, *Monatsh.*, **14**, 519 (1893).

[5] Dennis and Hance, THIS JOURNAL, **44**, 307 (1922).

[6] Treadwell and Mussler, *Helv. Chim. Acta*, **5**, 812 (1922).

Experimental Part

The apparent solubility of germanium tetrachloride and of arsenious chloride in hydrochloric acid of various concentrations was determined in order to learn the concentration of acid most suitable for extraction purposes. The term "apparent solubility" is used advisedly since it cannot be said that no hydrolytic decomposition of the chlorides takes place on dissolving.

Materials.—Germanium tetrachloride was prepared from the mineral germanite. The mineral was decomposed by concentrated nitric acid. This served to remove the great bulk of copper, iron and sulfur, leaving a siliceous residue small in bulk and rich in germanium dioxide. The residue was treated with concentrated hydrochloric acid and germanium tetrachloride distilled and collected under iced water. Hydrolysis of the chloride gave the dioxide, which was contaminated with arsenic. This was removed by the sulfide method. The pure germanium sulfide obtained was hydrolytically converted to the dioxide[7] and the latter reconverted to the tetrachloride. No attempt was made to remove hydrogen chloride from the product since it was to be used in experiments in which it would be shaken with hydrochloric acid. The other materials were Baker's C. P. Analyzed Chemicals. Arsenic-free sulfuric and hydrochloric acids were used at all times when the avoidance of traces of this element was desired.

Methods of Analysis.—Determinations of germanium and separations of germanium from arsenic were made according to the method of Abrahams and Müller.[3] Arsenic was determined as magnesium pyroarsenate according to the method of McNabb.[8]

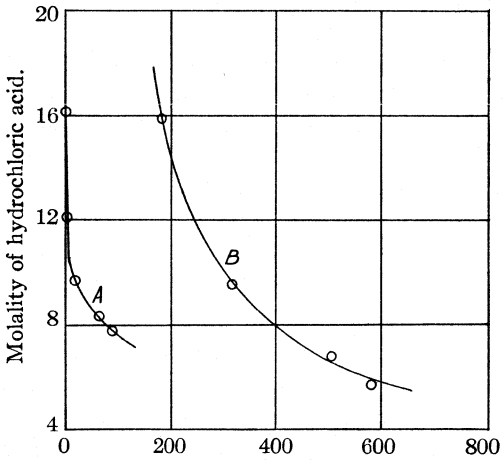


Fig. 1.—Curve A, germanium tetrachloride; Curve B, arsenious chloride.

Experimental Procedure.—Concentrated hydrochloric acid of known strength, and various solutions of the carefully diluted acid, were placed in 50-cc. sealing bottles and an excess of germanic chloride added to each one. The bottles were sealed and suspended in a thermostat maintained at 25 ± 0.02°. The bottles were shaken manually several times a day. After two weeks samples of the clear upper layers were taken for analysis. A similar series of determinations was made in which arsenious chloride was the solute. The results of the analyses are given in Tables I and II, and represented graphically in Fig. 1.

The solubility of both chlorides increases as more dilute acid is used as

[7] Müller and Eisner, *Ind. Eng. Chem., Anal. Ed.*, **4**, 134 (1932).

[8] McNabb, THIS JOURNAL, **49**, 1451 (1927).

solvent. Germanic chloride is almost insoluble in the most concentrated acid used, while arsenious chloride has a very high solubility in the same solvent. The diluted acid, which dissolves almost one hundred times as much germanium tetrachloride as the concentrated acid, dissolves only about twice as much arsenious chloride as the concentrated acid. This is clearly shown in Fig. 1. Concentrated hydrochloric acid is thus most suitable for the extraction of arsenious chloride from germanium tetrachloride.

TABLE I

APPARENT SOLUBILITY OF GERMANIC CHLORIDE IN HYDROCHLORIC ACID AT 25°

	Molality of HCl	G. $GeCl_4$/1000 g. solvent	Molality of $GeCl_4$
1	16.14	0.882	0.00411
2	12.08	1.826	.00852
3	9.72	17.84	.0832
4	8.32	61.83	.288
5	7.77	85.36	.398

TABLE II

APPARENT SOLUBILITY OF ARSENIOUS CHLORIDE IN HYDROCHLORIC ACID AT 25°

	Molality of HCl	G. $AsCl_3$/1000 g. solvent	Molality of $AsCl_3$
1	15.87	181.5	1.00
2	9.52	316.7	1.75
3	6.80	506.0	2.79
4	5.71	582.5	3.21

Since germanium tetrachloride proved to be so slightly soluble in concentrated hydrochloric acid it seemed possible that it would be precipitated from an aqueous germanium dioxide solution on saturation with hydrogen chloride. The production of liquid germanic chloride without distillation in the reversal of the hydrolysis reaction

$$GeCl_4 + 2H_2O = GeO_2 + 4HCl$$

has not been reported. The experiment is also of interest as a further test of the solubility of germanic chloride in concentrated hydrochloric acid. A solution of germanium dioxide was chilled in crushed ice and saturated with hydrogen chloride. Germanium tetrachloride was produced, separated from the hydrochloric acid by means of a separatory funnel, and identified by its boiling point. The hydrochloric acid was analyzed for its germanium content. It contained only 0.348 g. of germanium tetrachloride per 1000 g. of solvent, which compares favorably with values obtained later for the solubility of germanium tetrachloride in concentrated hydrochloric acid at 0° (see Table IV).

The Distribution of Arsenious Chloride between Germanium Tetrachloride and Concentrated Hydrochloric Acid

Apparatus.—On account of the high vapor pressures of the liquids involved it was necessary to work at a low temperature. A jacketed

separatory funnel was obtained for use as the vessel in which equilibrium conditions were attained. The outer jacket could be packed with crushed ice, keeping the inner compartment at 0°. The inner compartment was cylindrical in shape and set off center, causing one side to nearly touch the wall of the outer jacket. In this way the ice did not prevent vision into the inner compartment.

Experimental Procedure.—Approximately 10 cc. of arsenious chloride, 50 cc. of germanium tetrachloride and 75 cc. of concentrated hydrochloric acid were placed in the apparatus. The acid used contained 36.63% hydrogen chloride. The apparatus was shaken for two minutes and then allowed to stand for three minutes. This was repeated for an hour and a half, then the apparatus was allowed to stand for half an hour to give complete settling of the germanium tetrachloride layer. Samples of the upper hydrochloric acid layer were sealed in thin-walled glass bulbs for accurate weighing. It was not necessary to weigh samples of the germanium tetrachloride layer. Portions were run under cold water and allowed to hydrolyze. Pellets of pure sodium hydroxide were added slowly until the solution reacted alkaline to phenolphthalein. Warming caused rapid solution of the germanium dioxide which had resulted from the hydrolysis of the chloride. The solutions thus obtained were analyzed for both arsenic and germanium.

After the first set of samples had been taken the hydrochloric acid layer was siphoned out of the apparatus and replaced by fresh acid. Repetition of the shaking and sampling procedure gave a second set of samples in which the amounts of arsenious chloride present in the two layers were necessarily smaller. In the same way a third set of samples was obtained. This made possible the determination and comparison of values for the distribution coefficient obtained with varying amounts of arsenious chloride distributed.

Results of the analyses and the values of the distribution coefficient are given in Table III. Variation of the distribution coefficient is expressed graphically in Fig. 2. Experiments 4A and 4B were carried out under a different procedure. Germanium tetrachloride, arsenious chloride and concentrated hydrochloric acid were placed together and sealed in large bulbs. These were fastened to a mechanical shaker placed in a

TABLE III

DISTRIBUTION COEFFICIENT AT 0°

	Molality of $AsCl_3$ in HCl layer, M_1	Molality of $AsCl_3$ in $GeCl_4$ layer, M_2	$K = M_1/M_2$
1	0.3298	0.3571	0.9235
2	.1707	.1617	1.056
3	.08012	.06489	1.235
4A	.2323	.2468	0.9413
4B	.2356	.2475	.9519

cold room regulated at 0°, with a maximum variation of 5°. After five days the bulbs were taken off the shaker and kept in crushed ice, still in the cold room, for an additional twenty-four hours. This gave a final equilibrium temperature of 0°. Samples of the two layers were taken as in the previous experiments.

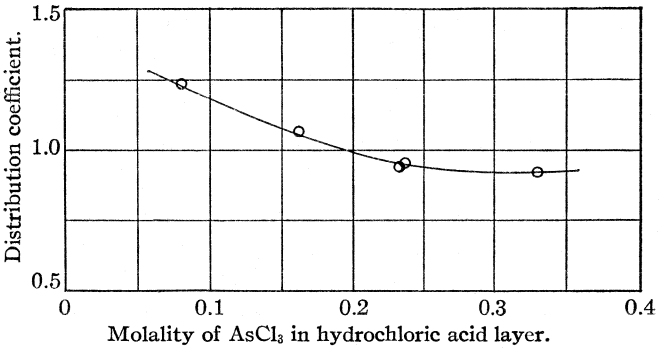


Fig. 2.—Variation of the distribution coefficient with the amount of arsenious chloride distributed between concentrated hydrochloric acid and germanium tetrachloride at 0°.

The values of the distribution coefficient vary inversely with the amounts of arsenious chloride distributed between the two layers. The rate of extraction, removal of arsenious chloride from germanic chloride, increases as the extraction proceeds, although the coefficient is small in all cases. The fact that the values obtained in experiments 4A and 4B, in which six days were allowed for the attainment of equilibrium, fall in the proper relation to the other values, is an indication that equilibrium conditions had been reached in all experiments. This is clearly shown in Fig. 2.

The concentration of germanium tetrachloride in the concentrated hydrochloric acid layers was determined. The results are given in Table IV. The solubility of germanic chloride in concentrated hydrochloric acid at 0° is shown to be considerably less than at 25° (compare No. 1, Table I).

TABLE IV

CONCENTRATION OF GERMANIC CHLORIDE IN THE CONCENTRATED HYDROCHLORIC ACID LAYERS AT 0°

G. concd. HCl + $GeCl_4$	$GeCl_4$ found, g.	$GeCl_4$, %	Average of best 3	Molality of $GeCl_4$
10.2960	0.00291	0.0283		
8.1893	.00322	.0393		
13.8241	.00502	.0363		
12.5074	.00455	.0364	0.0373	0.00174

Purification Experiment

The coefficient for the distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride is so small that a sample of germanic chloride containing arsenious chloride must be shaken with several portions of acid in order to remove the arsenic completely. This can be done without loss of much germanium since the solubility of the chloride in concentrated hydrochloric acid at 25° is sufficiently low to allow the use of a liter of acid with an accompanying loss of only 1 g. of germanium tetrachloride. At 0° the solubility is less than half as much. A purification experiment was made using the apparatus shown in Fig. 3. Impure germanic chloride and concentrated hydrochloric acid are shaken together in chamber A, allowed to separate into two layers, and the lower germanic chloride layer then run into chamber B. The acid layer is poured out of the apparatus and the germanic chloride run back into A from B, after proper adjustment of the three-way stopcock at C. Fresh acid is now added. The process involves inversion of the apparatus and removal of the stopper at D while the acid is being poured out.

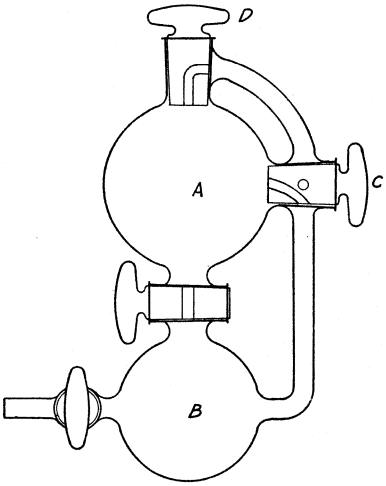


Fig. 3.—Extraction apparatus.

Approximately 35 cc. of germanic chloride containing 1.16% of arsenious chloride was treated with 70 cc. of chilled acid. The same amount of acid was used for the second extraction and 100 cc. in each of the successive treatments, each extraction requiring about five minutes. After the eighth extraction the acid no longer gave a test for arsenic and no arsenic could be detected in the germanium tetrachloride. On the basis of the small amount of arsenic required to discolor germanium sulfide,[3] and since the last portion of acid used gave a pure germanium sulfide precipitate when treated with hydrogen sulfide, it was calculated that the germanium tetrachloride layer could not have contained more than one part of arsenious chloride for each two million parts of germanium tetrachloride.

Experiments with the Chlorides of Antimony, Tin and Titanium.—A study of the behavior of chlorides of elements closely related to germanium and arsenic, with concentrated hydrochloric acid in the presence of germanium tetrachloride, is interesting. Antimony pentachloride, stannic chloride and titanium tetrachloride were chosen. These are known to be soluble in concentrated hydrochloric acid.

Approximately 25 cc. of germanic chloride was placed in the jacketed

separatory funnel and 1 cc. of antimony pentachloride added. This caused a slight turbidity which disappeared on treatment with 100 cc. of chilled acid. The apparatus was kept cold, shaken for fifteen minutes, and allowed to stand for thirty minutes. Portions of the germanic chloride layer were drawn off under cold water and the resulting solutions tested with hydrogen sulfide. No antimony could be detected. Similar experiments in which germanic chloride had been contaminated with stannic chloride and titanium tetrachloride resulted in the complete removal of these substances from germanium tetrachloride by a single extraction with concentrated hydrochloric acid.

Discussion of Results

The insolubility of germanium tetrachloride in concentrated hydrochloric acid is a characteristic difference in behavior from that of the tetrachlorides of titanium, tin and lead. These compounds are soluble in concentrated hydrochloric acid with formation of complex chloro acids of the type H_2MeCl_6. The corresponding germanium chloro acid has not been prepared. This behavior of germanic chloride is not only an interesting distinction from the anhydrous chlorides of its type, but also likens germanic chloride to the similarly inactive tetrachloride of carbon. The complete removal of the chlorides of antimony, tin and titanium from germanic chloride in one treatment with concentrated hydrochloric acid is an interesting distinction from the behavior of arsenic. This can only be well explained by the assumption of a definite formation of the chloro acids of these elements, which must be insoluble in the germanium tetrachloride layer.

Sufficient data for the calculation of the constant for the distribution of arsenious chloride between concentrated hydrochloric acid and germanic chloride are not available. The constant could only be calculated provided the concentration of simple arsenious chloride molecules in each layer were known. The values for the coefficient reported here were calculated from the total concentration of arsenic found in each layer. At present there is no information available regarding the ionization or possible association of arsenious chloride dissolved in germanium tetrachloride or concentrated hydrochloric acid. The actual conditions existing in these systems may be the subject of further investigation.

If proper apparatus for the preparation of large quantities of pure germanium tetrachloride by the distillation method is not available, the method of extracting arsenious chloride by means of cold concentrated hydrochloric acid may be conveniently used.

Summary

1. Arsenious chloride can be removed completely from germanium tetrachloride by extraction with concentrated hydrochloric acid.

2. The apparent solubility of germanium tetrachloride, and of arsenious chloride, in hydrochloric acid of various concentrations, has been determined. Germanium tetrachloride is practically insoluble in concentrated hydrochloric acid.

3. The distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride has been studied.

4. The chlorides of antimony, tin and titanium may be removed from germanium tetrachloride by a single extraction with concentrated hydrochloric acid.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PHOTOLYSIS OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION

BY LAWRENCE JOSEPH HEIDT

RECEIVED APRIL 26, 1932 PUBLISHED JULY 6, 1932

Quantum yields of the photolysis of hydrogen peroxide in aqueous solution as reported in the literature vary from 4 to 500. Rice and Kilpatrick[1] have suggested that dust-free solutions from which all surface effects have been eliminated should give a quantum yield of unity. Allmand and Style[2] found that the quantum yield decreases from 500 to 20 as the intensity of light increases.

Investigations of the photolysis prior to 1929 have been reviewed and discussed by Kistiakowsky[3] and by Griffith and McKeown.[4] Kornfeld[5] suggests the dissociation $H_2O_2 \longrightarrow H^+ + OOH^-$ in explaining her results. Urey, Dawsey and Rice[6] favor the photolysis $H_2O_2 \xrightarrow{h\nu} H_2O + (O)$. In the present investigation a quantitative study of the photolysis in monochromatic light was made to ascertain whether secondary effects can be eliminated to such an extent that the photolysis can be further studied profitably from a theoretical standpoint.

Materials.—General Chemical Co. superoxol (Code B, At 1788) was purified by distillation in an all-Pyrex still, at a pressure of 25 mm. in the presence of an excess of C. P., silver sulfate. The receiving flask at 0° was of

[1] Rice and Kilpatrick, *J. Phys. Chem.*, **31**, 1507 (1927).

[2] (a) Allmand and Style, *J. Chem. Soc.*, 596 (1930); (b) *ibid.*, 606 (1930).

[3] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 173–177.

[4] Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Green and Co., New York, 1929, pp. 459–461.

[5] Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921).

[6] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929).

quartz. Conductivity water for dilution was made by redistillation of distilled water first in a tin and then in an all quartz still. Sulfuric acid was made by dissolving in a quartz flask at 0° the white crystals of acid from 30% reagent quality fuming sulfuric acid in conductivity water. Solutions of the above purified materials were kept in covered quartz flasks. Potassium permanganate, C. P., was not subjected to further purification.

Purification of materials and all experiments were carried out in a laboratory comparatively free from dust. It had no windows and was isolated from chemical fumes. The laboratory air was filtered. All cells and glassware were cleaned with chromic acid and thoroughly rinsed with conductivity water.

Experimental Procedure

The light source, monochromator and radiometric procedure have been described.[7]

Absolute energy measurements were determined by reference to U. S. Bureau of Standards lamp C 44. They were checked against determinations of the decomposition of uranyl oxalate in the same cell using the data of Leighton and Forbes.[8]

A two compartment (9 cm. × 1 cm. × 1 cm.) rectangular quartz cell, all seams fused, was used as the reaction vessel. It was placed flush against the exit slit (0.6 mm. × 20.0 mm.) so that all the light from this slit was intercepted by the front windows of either compartment. Special precautions were taken to have the center of the beam pass through the center of the reaction compartment; otherwise results were erratic and gave higher values of the quantum yield, particularly if the beam grazed a side wall. Photolyses were carried out at 313 mμ and 28 ± 2° in only one compartment at a time, thus eliminating corrections for the dark reaction taking place under otherwise identical conditions in the other compartment. The dark reaction, however, was generally negligible.

Analyses were carried out volumetrically using 0.02 *N* potassium permanganate standardized against sodium oxalate and oxalic acid. An excess of sulfuric acid was always present. Extra care was taken to prevent surfaces in contact with the hydrogen peroxide from rubbing together, and to add the titer always at the same rate; otherwise, analyses were not reproducible.

The "*P*H" of the solutions was determined by the use of a glass electrode apparatus[9] kindly furnished by Dr. Hazel. The values should be considered only as qualitative until the reliability of the glass electrode for solutions of this type is further established.

[7] (a) Daniels and Heidt, THIS JOURNAL, **54**, 2381 (1932); (b) Heidt and Daniels, *ibid.*, **54**, 2384 (1932).

[8] Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

[9] Hazel and Sorum, *ibid.*, **53**, 49 (1931).

Data and Discussion

Results of the photolyses are summarized in the table. Concentration of hydrogen peroxide is expressed in moles per liter. Data for one photolysis for each series are shown and check determinations of the quantum yield, Φ, are given in parentheses. The average quantum yield, Φ av., of the series is given in the last column. In series A, where the original peroxide containing an inhibitor was not purified, a strong blue fluorescence was noted throughout the solution.

TABLE I

Series	$[H_2O_2]$	$[H_2SO_4]$	"P_H"	I/I_0	Time of photolysis in sec. $\times 10^{-3}$	Quanta absorbed $\times 10^{-19}$	Molecules decomposed $\times 10^{-19}$	Φ	Φ av.
A	1.77	0.0	3.0	89	7.2	7.9	14.2	1.8 (1.7 0.9)	1.5
B	2.36	0.0	3.6	91	7.2	7.0	8.0	1.1 (1.1 1.1)	1.1
C	4.20	0.0	2.5	98	7.2	3.5	6.8	2.0 (3.1 2.1)	2.4
D	3.70	1.3	−1.0	96	14.4	8.2	15.6	1.9 (1.9 1.3)	1.7
E	3.72	4.1	−1.8	95	14.4	5.6	11.2	2.0 (1.3 2.1 1.8)	1.8
F	4.48	1.3	−1.5	98	10.8	6.6	6.4	1.0 (1.6 2.0 2.1)	1.7

It is evident from the table that a quantum yield approaching unity has been obtained, substantiating the predictions of Rice and Kilpatrick[1] for dust-free solutions and those of Griffith and McKeown[4] for radiation of high intensity. The intensity per square millimeter was of the order of 1000 times that of Allmand and Style[2b] in their experiments with filters. The data also show, almost within the limits of experimental error, that Φ tends to increase with the concentration of hydrogen peroxide and to decrease with the addition of sulfuric acid. Results obtained a year later independently by Mr. Harrison Holmes and the author are in general agreement with the above.

Calculations based on the data of the table show that the extinction coefficient, $\epsilon(1/cd \log I_0/I$ where c is expressed in moles per liter and d in cm.), tends to decrease with an increase in $[H_2O_2]$ and in $[H_2SO_4]$. The reaction cell used in these experiments was irregular but the thickness was approximately 1 cm. and relative values of ϵ are accurate to 5%.

Using the method of Forbes, Heidt and Boissonnas[10] for measuring extinction coefficients, the following was obtained. In a given cell for 2.36 molar H_2O_2, $\epsilon_{313\ m\mu} = 0.44$; for 2.36 molar H_2O_2 in 2.6 molar H_2SO_4, $\epsilon_{313\ m\mu} = 0.41$ and on adding a slight excess of sodium hydroxide to 2.36 molar H_2O_2, $\epsilon_{313\ m\mu} = 1.14$. All measurements were taken before any noticeable decomposition had taken place. From this it appears that some chemical individual derived from hydrogen peroxide, possibly the ion OOH^-, has an extinction coefficient for λ 313 mμ greater than that of the peroxide. To draw definite conclusions, it is planned to make a detailed study of the dependence of ϵ on $[H_2O_2]$ and $[H^+]$. In later experiments

[10] Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).

with an improved cell $\epsilon_{313\ m\mu}$ was found to be 0.38 for molar hydrogen peroxide. This is in good agreement with the value 0.39 obtained by Allmand and Style.[2a]

The author desires to express his appreciation to Professor Farrington Daniels for his help and guidance in this investigation, and to the Research Committee of the University of Wisconsin for substantial aid.

Summary

1. A quantum yield approaching unity as the concentration of hydrogen peroxide is decreased has been obtained for its photolysis in aqueous solution at 28 ± 2° using light of high intensity at 313 mμ from a monochromator.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, DEPARTMENT OF AGRONOMY OF THE OHIO AGRICULTURAL EXPERIMENT STATION]

THE OPTICAL CRYSTALLOGRAPHIC DESCRIPTION OF THE PHENYLOSAZONES AND OTHER DERIVATIVES OF CERTAIN SUGARS[1]

BY VINCENT H. MORRIS

RECEIVED APRIL 27, 1932 PUBLISHED JULY 6, 1932

Introduction

The identification of sugars which have been isolated from plants or plant products is a constantly recurring problem. The usual method of attack consists of preparing insoluble derivatives of the sugars in more or less pure crystalline form and identifying these derivatives through their melting points, optical rotation, microscopic observation of crystal form, etc. Since the presence of very small quantities of impurities is sufficient to make melting points misleading, as well as to influence the crystal form, positive identification through these characteristics is sometimes difficult. In searching for some other means, that suggested by Wright,[2] based on the optical properties of the crystalline derivatives, seemed to offer promise of being such a valuable tool in the identification of sugars that a study of certain derivatives of some of the more common sugars was undertaken.

Materials.—The sugars investigated were glucose, fructose, mannose, galactose, arabinose, xylose and maltose. The derivatives used were the phenylosazones of five of these and the following additional compounds:

[1] This study was carried out under the direction of Dr. H. C. Sampson and Dr. W. G. McCaughey, Departments of Botany and Mineralogy, respectively, The Ohio State University, and presented in partial fulfilment of the requirements of the degree of Doctor of Philosophy to the Faculty of the Graduate School of The Ohio State University. Original manuscript received October 23, 1931.

[2] Wright, THIS JOURNAL, **38**, 1647 (1916).

potassium hydrogen saccharate, fructose methylphenylosazone, mannose phenylhydrazone, mucic acid, arabinose diphenylhydrazone and cadmium bromide xylonate. The phenylosazones, potassium hydrogen saccharate and mannose hydrazone were prepared according to Morrow,[3] mucic acid and arabinose diphenylhydrazone according to Van der Haar,[4] fructose methylphenylosazone according to Neuberg,[5] and cadmium bromide xylonate according to Bertrand and Thomas.[6]

Methods.—The immersion method of examination used by mineralogists and petrographers for many years was employed. The light used in measuring refractive indices and extinction angles was obtained by passing light from a 400-watt Mazda C bulb through two Corning glass ray filters, G584J and G34. These filters transmit light from 540$\mu\mu$ to 640$\mu\mu$ with a maximum at 580$\mu\mu$.

The phenylosazones and several of the other derivatives were obtained as such minute crystals that it was necessary to use an oil immersion objective in measuring the refractive indices.[7] The size of the crystals, together with the unusually high degree of dispersion shown by the crystals themselves and also by the methylene iodide solutions used in measuring the high indices, made this determination unusually difficult. The indices between 1.70 and 1.80 are accordingly accurate only to about ± 0.005, while those above 1.80 are accurate to ± 0.01. The indices below 1.70 are probably all correct within ± 0.002.

The optical axial angle was estimated from the curvature of the isogyre of an optic axis interference figure or by actual measurement of the distance between the axes, using a micrometer eyepiece. Since, with the equipment available and the type of material under examination, these methods only give approximations, the angles are reported as large, medium or small.

The optical crystallographic data are given in Table I. A determinative table for identification of five of the sugars by optical examination of their phenylosazones is given in Table II.

[3] Morrow, "Biochemical Laboratory Methods for Students of the Biological Sciences," John Wiley and Sons, New York, 1927.

[4] Van der Haar, "Anleitung zum Nachweis zur Trennung und Bestimmung der reinen und aus glucosiden usw. erhaltenen Monosaccharide und Aldehydsäuren," Gebrüder Borntraeger, Berlin, 1920.

[5] Neuberg, *Ber.*, **35**, 959 (1902).

[6] Bertrand and Thomas, "Practical Biological Chemistry," G. Bell and Sons, London, 1920.

[7] The immersion media for determining refractive indices below 1.65 were mixtures of a Halowax oil and mineral oil, for indices between 1.65–1.74 mixtures of the Halowax oil and methylene iodide and for those between 1.74–1.86 solutions of iodoform, tri-iodide of arsenic, tri-iodide of antimony, tetra-iodide of tin and sulfur in methylene iodide prepared according to Merwin, "Media of High Refraction for Refractive Index Determinations with the Microscope; also a Set of Permanent Standard Media of Lower Refraction," *J. Wash. Acad. Sci.*, **3**, 35 (1913).

TABLE I

OPTICAL CRYSTALLOGRAPHIC DATA FOR THE PHENYLOSAZONES AND OTHER DERIVATIVES OF CERTAIN SUGARS

Derivative Phenylosazones	Crystal system	Refractive indices α	β	γ	Optical character	Optic axial angle	Sign of elongation	Optical orientation	Crystal habit	Remarks
Glucose	M	1.755	1.780	1.850	+	Medium	±	$Y = b$ Axial plane 010	Needles, elongated || b flattened || 100	Characteristic blue, green, purple interference colors
Galactose	M	1.790	1.800	1.845	+	Small	−	$X \wedge c = 30°$ Axial plane 010	Blades, elongated || 100 flattened || 100	Orange and green interference colors
Arabinose	O	1.760	1.765	1.800	+	Small	+	$Z = Bxa = c$ Axial plane 100	Needles, elongated || c flattened || 100	Green and yellow interference colors
Xylose	O	1.725	1.760	1.805	+	Large	+	$Z = Bxa = c$ Axial plane 100	Needles, elongated || c flattened || 100	Green and yellow interference colors
Maltose	O	1.655	1.715	1.730	−	Small	+	$X = Bxa = b$ Axial plane 100	Blades, elongated || c flattened || 100	Green, yellow, orange interference colors
Other derivatives										
Potassium hydrogen saccharate	M	1.483	1.571	1.586	−	Medium		$X \wedge c = 42°$, $Y = b$ Axial plane 010	Tablets, elongated || 010 flattened || 100	Optic axis nearly $\perp$100
Fructose methyl-phenylosazone	O	1.589	1.603	1.82+	+	Small	−	$Z = Bxa = a$ Axial plane 010	Tablets, elongated || c flattened || 100	Pleochroic, X yellow, Y dark yellow, Z brown
Mannose phenyl-hydrazone	T	1.600	1.650	1.82±	+	Large		Optic axis nearly $\perp$001 Axial plane nearly bisects acute angle on 001	Rhomb-shaped tablets lying on 001, included angles of 106 and 74°	Acute angle sometimes truncated by small crystal face
Mucic acid	T	1.490*	1.600	1.610	−	Medium		Axial plane $\wedge$ elongation = 40° $X = Bxa$ = nearly $\perp$001	Rhomb-shaped tablets lying on 001, included angles of 94 and 86°	*Refractive index for α approximate only
Arabinose diphenyl-hydrazone	O	1.627	1.674	1.735	+	Large	±	$Z = Bxa = b$ Axial plane $\perp$010	Prisms, elongated || c	Faces present are prism, brachypinacoid, brachydome, macrodome; sometimes pyramid and basal pinacoid
Cadmium bromide xylonate	O	1.615	1.633	1.638	−	Small	+	$Z = Bxo = c$ Axial plane $\perp$110	Prisms, elongated || c lying on 110	Bisphenoid faces give characteristic boat shape to crystals.

TABLE II

DETERMINATIVE TABLE FOR IDENTIFICATIONS OF FIVE SUGARS BY OPTICAL EXAMINATION OF THEIR PHENYLOSAZONES

Observation	Sugar is
Immerse substance in liquid with $n = 1.730$	
Two n's (both crosswise) lower than liquid, = that of third	maltose
One n (crosswise) lower than liquid, other two much greater	xylose
All n's much higher than liquid, then:	
Immerse substance in liquid with $n = 1.790$	
Two n's (both crosswise) much lower than liquid, third slightly higher	arabinose
One n = liquid ($\pm 30°$ with elongation), others higher	galactose
Two n's less and one much greater, elongation $\pm$	glucose

WOOSTER, OHIO

NOTES

The Existence of the High-Temperature Form of Cristobalite at Room Temperature and the Crystallinity of Opal

BY J. W. GREIG

There has appeared recently an interesting letter from Levin and Ott[1] announcing that they have established, by means of x-rays, the existence of the high-temperature modification of cristobalite in a number of opals. So far as I am aware, the high-temperature modification of cristobalite has not before been shown to occur in nature at atmospheric temperatures. In my opinion, however, this form has, contrary to their statement, been shown to be present at room temperature in certain artificial products.

In the course of experimental determinations of points on the liquidus of silica, in systems of silica with other oxides, carried out at this Laboratory, study of the charges frequently shows that some of the cristobalite crystals embedded in the glass are sensibly isotropic, often in contrast to other birefringent ones in the same melt. This has been observed repeatedly by microscopists doing this work here and was explained by Andersen as due to some of the crystals of cristobalite failing to invert during cooling and so persisting in the high-temperature cubic modification.[2]

In connection with a study of the decomposition of cyanite, $Al_2O_3 \cdot SiO_2$, at high temperatures to give mullite, $3Al_2O_3 \cdot 2SiO_2$, and silica, I have investigated the question of the form in which the silica was present in the product of decomposition.[3] When first formed the products of the decomposition are so fine-grained that some question remains as to the nature of the silica, but with continued heating at high temperature it collects

[1] Levin and Ott, THIS JOURNAL, **54**, 828 (1932).

[2] O. Andersen, *Am. J. Sci.*, **39**, 418 (1915).

[3] J. W. Greig, *J. Am. Ceram. Soc.*, **8**, 478–481 (1925); *Am. J. Sci.*, **11**, 21–25 (1926).

into larger particles and is then definitely cristobalite. On cooling through the inversion temperature the cristobalite remains, as indicated by thermal studies, for the most part in the high-temperature form.

Although they do not explicitly say so, Levin and Ott have evidently based their opinion, that the high-temperature form of cristobalite has not before been shown to exist at room temperature, on the fact that Sosman, in his monograph on silica,[4] mentions only two reports to that effect and discusses both unfavorably. It is to be noted that the experiments described in these reports are of a somewhat different nature from those mentioned in the preceding paragraphs. In both these cases the cristobalite was already in the low-temperature form and supposedly free from any enclosing solid medium. As will appear later, this is probably an important difference. Sosman's remarks, quoted from p. 133, follow.

"Endell stated in 1912 that he had found the low-to-high inversion of cristobalite to be reversible with difficulty, and that rapid cooling after the crystals had been heated to above 220° left them in the isotropic high-form, from which the change" [to the low-temperature birefringent form] "at atmospheric temperature was a matter of some hours" (phrase in brackets mine).

"Schwarz has also stated that cristobalite after being heated about 15 minutes at 250° and then quickly cooled remains isotropic.

"These statements are in such direct contradiction to the numerous observations of all other investigators that it can hardly be admitted without further evidence that the phenomena observed were really due to a delayed inversion. It is easy to be mistaken on this point because cristobalite after passing through the inversion is very fine grained, and its birefringence, furthermore, is small, so that it may give a false appearance of being isotropic."

One must agree with Sosman that more evidence is needed before one can accept their conclusions as established, for their reported results are not in accord with general experience with cristobalite. The two forms of cristobalite are distinguishable by other properties than birefringence, yet no one, so far as I am aware, has since reported the same result, although many experimenters have studied cristobalite since 1912. It must, however, be noted that Sosman's suggested explanation cannot account for Endell's reported observations. It could indeed explain only the first part and would put anyone accepting it in a difficult position in respect to the second part. If one accepts it he must, to explain the reappearance at room temperature of the normal birefringent aspect, assume further that in this aggregate of cristobalite, already in the low-temperature form, individual crystals grew markedly in a few hours at room temperature.

[4] R. B. Sosman, "The Properties of Silica," American Chemical Society Monograph 37, 1927.

It is appropriate here to mention two additional sets of observations, so far unpublished, indicating that under certain conditions the high-temperature form of cristobalite may be brought to room temperature without inverting. The first of these is a confirmation of Andersen's opinion. I have examined literally hundreds of charges, similar to those described by Andersen, in which well-formed cristobalite crystals occur distributed in glass. It is quite normal to find, using crossed nicols, that sensibly isotropic cristobalite crystals as well as birefringent cristobalite crystals occur together in the same preparation. Since the inversion from the high-temperature to the low-temperature form is accompanied by a considerable decrease in volume, the high-temperature isotropic form should have the lower index of refraction. It should thus be possible, by this property, to differentiate them readily, if they were embedded in a medium with an intermediate index of refraction. In order to apply this test I have prepared suitable glasses with indices of refraction lower than those of the low-temperature form (*i. e.*, $n < 1.485$), and, by holding these at a temperature immediately under that of the cristobalite liquidus, have grown excellent faceted crystals of cristobalite in them. The cristobalite crystals in these glasses after cooling to room temperature were of both the isotropic and the birefringent kinds. The isotropic crystals had always a low index of refraction (not far from that of a glass $n = 1.46_6$), and were thus definitely differentiated from those that had inverted and that had therefore a higher index of refraction than the glass. Reëxamination of some of these preparations after they had stood for over three years at room temperature showed that sensibly isotropic crystals with this low index of refraction were still present. It is accordingly concluded that in these glasses cristobalite in the high-temperature form may be cooled to room temperature without inverting and will there remain in that form for an indefinite time.

In the case of certain silicate liquids it is extremely difficult to prevent the crystallization of cristobalite during cooling. When such liquids are chilled the cristobalite appears as small crystals thickly distributed throughout so that the quenched products vary, depending on the size and number of the crystals, from faintly opalescent to porcelain-like.[5] I have made heating and cooling curves on several such porcelain-like "glasses" using a differential apparatus sufficiently sensitive to detect the heat absorption or evolution accompanying the inversion of a fraction of the cristobalite present, yet these curves showed no trace of such heat effect. The cristobalite in them did not invert sharply on cooling through the inversion temperature.

In the cases that I have described, from my own experience, in which high-temperature cristobalite was cooled through the inversion tem-

[5] J. W. Greig, *Am. J. Sci.*, **13**, 40–44 (1927).

perature without inverting, the crystals were small and embedded in some solid medium: in one case intergrown with mullite crystals, in the other cases embedded in a siliceous glass. In the glasses with an index of refraction <1.485 mentioned above the glass immediately surrounding the crystals with the low index of refraction is, at room temperature, invariably birefringent, showing that it is strained. The relation of the vibration directions of the fast and slow rays in the strained glass to the enclosed crystal, together with the localization of the strain, indicate that the strain is due to a contraction of the crystal that is being resisted by the glass. The glass and crystal are therefore adhering. This strain fades out on heating but on cooling reappears, becoming evident at a temperature somewhat above that of the inversion, and increasing as the temperature is lowered. The glass surrounding the crystals that have inverted to the low-temperature form, on the other hand, is not strained, and in some cases it is even possible by careful microscopic work to see that a crack surrounds the crystal. The inversion and the breaking free of the crystal from the restraint of the glass are thus associated. Such crystals invert to the high-temperature form on heating and back again on cooling, as may readily be seen by watching them under the microscope during the process. It is probable, in view of the strong contrast between the behavior of the crystals mechanically attached to the surrounding glass and that of free crystals, whether surrounded by the glass as these are, or prepared by some other method and entirely separate, that the solid embedding medium exercises an important restraint on the inversion of the attached crystals.

Since the appearance of the letter by Levin and Ott, Dr. E. Posnjak has obtained an x-ray spectrogram, corresponding closely to that given by the high-temperature form of cristobalite, from a translucent amber-colored "resin opal" from Queretaro, Mexico. Dr. H. E. Merwin and I have examined this material under the microscope. It is then resolved into two parts, a matrix $n = 1.41$ and, thickly distributed through it, small particles of considerably higher index of refraction. In all likelihood these particles are the crystals giving rise to the x-ray pattern. If, as seems most probable, they are indeed the high-temperature form of cristobalite, they are probably another example of small crystals of cristobalite embedded in a medium failing to invert on cooling through the inversion temperature, for, on the basis of our present very limited knowledge, this is considered more probable than that the high-temperature form of cristobalite would crystallize in the temperature range in which the low-temperature form is the more stable.

GEOPHYSICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.

RECEIVED FEBRUARY 29, 1932
PUBLISHED JULY 6, 1932

The Preservation and Determination of Sodium Sulfocyanate

By Joseph Greenspan

Several recent improvements in the analytical determination of thiocyanates by oxidation with iodine in appropriate alkaline buffers permit of a more precise investigation of the kinetics of reactions involving thiocyanate ion.[1] In searching the literature for means of preventing mold formation in standard aqueous solutions of sodium thiocyanate, we were struck by the paucity of information regarding this salt.[2] We have found the following methods satisfactory.

Preservation.—The commercial c. p. salt was recrystallized from 95% alcohol. The addition of one drop of toluene per 100 cc. of approximately 0.02 *M* solutions completely prevented mold growth and loss of titer for a period of at least three weeks, whereas mold growth developed in the absence of toluene. Titration after two weeks of standing with toluene preservative gave a value of 0.01982 *M;* after three weeks, 0.01982 *M*.

Analytical.—The ammonia–ammonium salt buffer recommended by Pagel and Koch[3] developed iodine absorption after standing for several days, giving titer values of 13.38, 17.68, 15.92 cc. against the calculated 20.83, 20.64, 20.54 cc., respectively, although accurately concordant results were obtained with fresh buffer, giving 18.71, 20.43 cc. *vs.* calculated 18.67, 20.46 cc. The authors mention that traces of nickel, cobalt and manganese produce erratic results. Our solutions were kept in Non-Sol bottles.

Schwicker's[4] ammonium borate buffer method, as modified by Pagel and Ames,[5] yielded a black precipitate, presumably an iodide of nitrogen, which disappeared upon subsequent acidification. This method was therefore rejected in favor of that employing a borax buffer,[5] which yielded accurate and consistent values, 40.51, 40.53 cc. *vs.* calculated 40.49, 40.51 cc.

[1] See La Mer and Greenspan, This Journal, **54**, 2739 (1932).

[2] Beilstein, 4th ed., Vol. III, p. 150; Erstes Erganzungswerk, Vol. III, p. 66.

[3] Pagel and Koch, This Journal, **53**, 1774 (1931).

[4] Schwicker, *Z. anal. Chem.*, **77**, 278–280 (1929).

[5] Pagel and Ames, This Journal, **52**, 2698 (1930).

Contribution from the
Department of Chemistry
Columbia University
New York, N. Y.

Received March 11, 1932
Published July 6, 1932

The Equilibrium of Para and Ortho Hydrogen

By Roy W. Harkness and W. Edwards Deming

Investigators in several laboratories are studying the transition of para to ortho hydrogen. In most of this work it is desirable to know the equilibrium ratio at different temperatures. There appears to be no accessible tabulation of this ratio, and it seems desirable to publish a table calculated

from Dennison's[1] equation, covering the range 20 to 273°K. Between these temperatures the equilibrium mixture changes from 99.82% para to 25.13%. In the accompanying table we give the ratio of para to ortho hydrogen and the percentage amount of para hydrogen at a sufficient number of temperatures for ordinary purposes. In the liquid air range values are given at every degree.

RATIO AND PERCENTAGE OF PARA HYDROGEN IN AN EQUILIBRIUM MIXTURE AT VARIOUS TEMPERATURES, CALCULATED FROM THE EQUATION

T, °K.	Ratio para:ortho	Para hydrogen, %	T, °K.	Ratio para:ortho	Para hydrogen, %	T, °K.	Ratio para:ortho	Para hydrogen, %
20	544.8	99.82	76	1.046	51.13	95	0.6801	40.48
21	363.5	99.73	77	1.017	50.41	100	.6262	38.51
22	251.6	99.60	78	0.9894	49.73	105	.5829	36.82
23	179.8	99.45	79	.9626	49.05	110	.5456	35.30
24	132.2	99.25	80	.9377	48.39	115	.5152	34.00
25	99.57	99.01	81	.9140	47.75	120	.4897	32.87
30	32.07	96.98	82	.8916	47.13	130	.4498	31.03
35	14.28	93.45	83	.8702	46.53	140	.4208	29.62
40	7.780	88.61	84	.8500	45.95	150	.3994	28.54
45	4.853	82.91	85	.8307	45.37	160	.3835	27.72
50	3.327	76.89	86	.8123	44.82	170	.3715	27.09
55	2.443	70.96	87	.7981	44.39	190	.3555	26.23
60	1.890	65.39	88	.7781	43.76	210	.3463	25.72
65	1.521	60.33	89	.7621	43.25	230	.3409	25.42
70	1.264	55.83	90	.7469	42.75	250	.3377	25.24
75	1.077	51.86	91	.7323	42.27	273	.3357	25.13

The ratio of para to ortho hydrogen, as given by Dennison, is

$$\frac{1 + 5e^{-6x} + 9e^{-20x} + 13e^{-42x} + \ldots}{9e^{-2x} + 21e^{-12x} + 48e^{-30x} + \ldots}$$

wherein $x = h^2/8\pi^2 JkT$. We have adopted the following values, in C. G. S. units: $h = 6.547 \times 10^{-27}$, $k = 1.371 \times 10^{-16}$, $J = 0.466 \times 10^{-40}$, so that $xT = 84.977$. J is the moment of inertia of the hydrogen molecule, and the value $(0.466 \pm 0.001)\ 10^{-40}$ was estimated by Birge and Jeppesen.[2] Increasing J by 0.001×10^{-40} lowers the calculated percentage of para hydrogen 0.13 per cent. in the central portion of the curve and much less at the end portions. The series in the numerator and denominator converge rapidly over the temperature range used; the expression written above contains all the terms needed for the accuracy of the accompanying table.

Eucken and Hiller[3] published six values of the ratio para : ortho hydrogen, at T = 21.2, 28.3, 42.5, 60.0, 85, 170, which agree with the entries in our table except at their two highest temperatures, $T = 85$ and 170°.

[1] D. M. Dennison, *Proc. Roy. Soc.* (London), **A115**, 483 (1927).

[2] R. T. Birge and C. R. Jeppesen, *Nature*, **125**, 463 (1930).

[3] Eucken and Hiller, *Z. physik. Chem.*, **B4**, 142 (1929).

At $T = 85°$ they give 48.0%, whereas we find 45.4; at $T = 170°$ they give 25.3, whereas we find 27.1. They presumably calculated their values

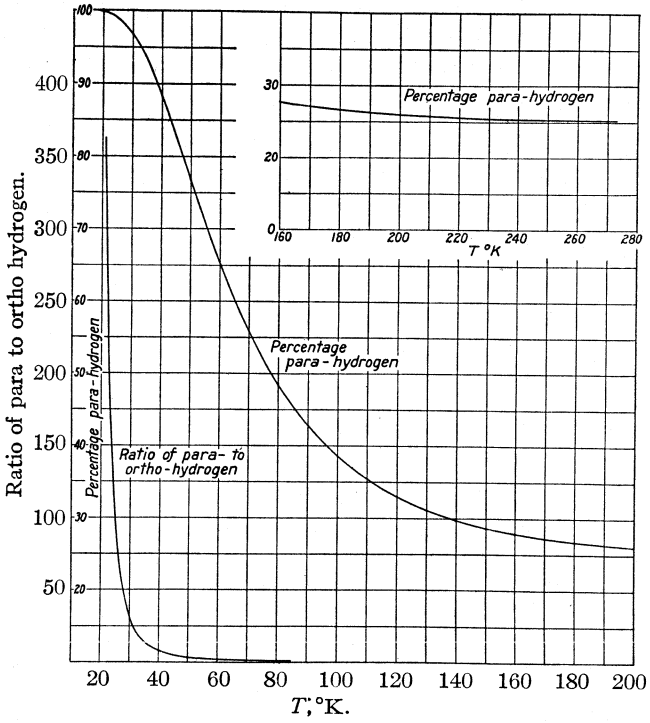


Fig. 1.

from Dennison's equation. We know of no explanation for this discrepancy. They used 0.467×10^{-40} for J, so it is not to be found there.

CONTRIBUTION FROM FERTILIZER AND
FIXED NITROGEN INVESTIGATIONS
BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.

RECEIVED MARCH 23, 1932
PUBLISHED JULY 6, 1932

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

IODIMETRIC TITRATION OF SEMICARBAZIDE[1]

BY PAUL D. BARTLETT

RECEIVED JANUARY 23, 1932 PUBLISHED JULY 6, 1932

The reaction of compounds containing the carbonyl group with nitrogen bases such as phenylhydrazine, semicarbazide and hydroxylamine, is one of the most general reactions of organic chemistry. A convenient and exact titration method for one of these nitrogen reagents therefore opens an important type reaction to quantitative study. Perhaps the most favorable case of this reaction for investigation is the formation of semicarbazones

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}O + H_2NNHCONH_2 \rightleftharpoons \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}NNHCONH_2 + H_2O$$

This is so because the semicarbazones crystallize well and are conveniently water-soluble, also because semicarbazide is not rapidly autoxidized. The present paper describes a titration method for semicarbazide which has been applied to the study of rates and equilibria in semicarbazone formation.[1a]

Dilute aqueous semicarbazide has been found to react quantitatively with iodine in the proportion of four atoms of iodine to one molecule of semicarbazide. The reaction, which is attended by effervescence except at high dilution, is probably as follows

$$H_2NNHCONH_2 + 2I_2 + H_2O \longrightarrow N_2 + CO_2 + NH_4I + 3HI$$

In this reaction semicarbazide is analogous to phenylhydrazine,[2] which reacts with iodine in the same proportion, and behaves differently from hydroxylamine, whose iodine equivalent varies with the concentration.[3]

Phenylhydrazine is inconvenient for reaction velocity studies because it and some of the phenylhydrazones are readily oxidized by the air. Just as semicarbazide is more stable in air than phenylhydrazine, so it is less rapidly attacked by iodine. Phenylhydrazine hydrochloride can be titrated with iodine, but the reaction between iodine and semicarbazide hydrochloride is very slow. Some rough tests were therefore made of the rate of this reaction in buffer solutions of different P_H values, in order to determine the necessary conditions for quantitative reaction within the time of a titration.

Reaction Rate as a Function of P_H.—Small samples of iodine and semi-

[1] From a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Harvard University in 1931.

[1a] Conant and Bartlett, THIS JOURNAL, **54**, 2881 (1932).

[2] E. Meyer, *J. prakt. Chem.*, [2] **36**, 115 (1887).

[3] Ölander, *Z. physik. Chem.*, **129**, 1 (1927).

carbazide hydrochloride were added in equivalent amounts to 20 cc. of 0.5 M buffer solutions diluted to 70 cc., kept in a thermostat at 25.00 ± 0.01°. Titrations were made with thiosulfate at short intervals. In all cases it was provisionally assumed that throughout the reaction one molecule of semicarbazide had disappeared for each four atoms of iodine which had reacted. The reciprocal of the semicarbazide concentration, calculated on this basis, increased linearly with time, showing that the reaction rate is controlled by a bimolecular step. Consistent results are obtained by the formulation

$$-dx/dt = kx \cdot 2x = 2kx^2$$

where t is the time in minutes, x is the concentration of semicarbazide and $2x$ is the concentration of iodine in moles per liter. The values of k are computed from the experimental data by the integrated form

$$2k = \frac{1}{t}\left[\frac{1}{x} - \frac{1}{x_0}\right]$$

x_0 being the initial concentration of the semicarbazide.

Table I gives the experimental data and the values of k for these runs at 25°. In these, x_0 is 0.000238, so that $1/x_0$ is 4200. The iodine solution used was 0.0336 N (0.0168 M). The figures in the column headed "Iodine" refer to the amount of iodine found in the reacting solution at the time of titration, expressed in cc. of stock solution.

TABLE I

RATE OF REACTION OF IODINE WITH SEMICARBAZIDE AT 25.00 ± .01°

P_H	Minutes	Iodine	$1/x$	$(1/x - 1/x_0)$	k
1.48	0.93	1.63	5610	1410	750
	3.23	1.01	9055	4855	750
	4.25	0.89	10300	6100	720
	6.02	.70	13065	8865	730
2.02	0.30	1.68	5450	1250	2080
	.98	1.17	7810	3610	1840
	1.47	0.86	10640	6440	2190
	1.95	.70	13060	8860	2270
2.45	0.37	1.11	8240	4040	5410
	.63	0.86	10640	6440	5100
	1.25	.50	18300	14100	5640
	1.68	.39	23450	19250	5720
3.01	0.16	0.75	12200	8000	25000
	.27	.52	17600	13400	24800

At P_H 3 the reaction has become almost too fast to measure, but the rates can be followed into solutions of higher P_H values by measurements at 0°. In these runs (summarized in Table II) x_0 = 0.000184 and $1/x_0$ = 5435.

TABLE II

RATE OF REACTION OF IODINE WITH SEMICARBAZIDE AT 0.1 ± 0.1°

P_H	Minutes	Iodine	$1/x$	$(1/x - 1/x_0)$	k
3.01	1.02	1.63	7900	2465	1200
	2.00	1.01	11110	5675	1310
	3.12	0.89	13620	8185	1410
	3.97	.70	15320	9885	1230
3.57	0.48	1.19	10430	4995	5200
	.96	0.78	15920	10485	5450
	1.21	.68	18245	12810	5290
	1.76	.59	21000	15565	(4430)
	1.88	.50	24810	19375	5150
5.01	0.18	.68	18250	12815	35600
	.44	.38	32700	27265	31000
7.08	.10	.25	49600	44400	180000
	.15	.23	54000	48800	248000

The chemical interpretation of a measurable first step followed by an immediate second step may be as follows

Step 1 $H_2NCONHNH_2 + I_2 \longrightarrow H_2NCONHNHI + HI$ (measurable)
Step 2 $H_2NCONHNHI + H_2O + I_2 \longrightarrow N_2 + NH_4I + 2HI + CO_2$ (immediate)

The dependence of the reaction rate upon the P_H would also be explained if, according to this picture, it is the free, non-ionized form of semicarbazide which reacts. We should then expect the rate constant to be proportional to the fraction of the semicarbazide which is present in the non-ionized form at the P_H of the reaction. This is shown to be true up to P_H 5 by dividing each value of k by that fraction, which we define as

$$F = \frac{(H_2NCONHNH_2)}{(NH_2CONHNH_2) + (H_2NCONHNH_3^+)}$$

Substituting the values for the semicarbazide positive ion (see below) $pK_A = 3.68$ at 25° and 4.40 at 0°, in the equation

$$pK_A - P_H = \log \frac{(H_2NCONHNH_3^+)}{(H_2NCONHNH_2)} = \log (1/F - 1)$$

we find values of F as shown in Table III.

Within the accuracy of the rate determinations, the corrected velocity constant k/F is independent of P_H up to P_H 5. This constancy through a set of buffer solutions involving different acids at different concentrations demonstrates the absence at these P_H values of any considerable catalysis by either acidic or basic substances in the buffers. On the other hand, rough as the measurements at P_H 7 are, they show clearly that there is an increase of about five-fold over the value of k/F in the other buffers at 0°. This is probably due to an independent hypoiodite reaction, analogous to the replacement of amide hydrogen by halogen, and yielding the same product as Step 1.

TABLE III

VELOCITY CONSTANTS REFERRED TO FREE SEMICARBAZIDE

Temp.	P_H	$(pK_A - P_H)$	$(1/F - 1)$	$1/F$	k	k/F
25°	1.48	2.20	159	160	740	118000
	2.02	1.66	45.7	46.7	2090	98000
	2.45	1.23	17.0	18.0	5470	99000
	3.01	0.67	4.68	5.68	24900	141000
					Average at 25°	115000
0°	3.01	1.39	24.6	25.6	1290	33000
	3.57	0.83	6.76	7.76	5270	41000
	5.01	− .61	0.246	1.25	33300	42000
	7.08	−2.68	.002	1.00	214000	214000
				Average at 0° (omitting P_H 7.08)		39000

Conditions of Titration.—This acceleration makes the reaction an acceptable titration method at P_H 7. Using the procedure described below, 99.9% of the semicarbazide present reacts with iodine in three seconds.

Experiments on the rate of reaction of iodine with semicarbazones will be described in a later communication.[1a] In no case is this reaction rapid enough to be a significant source of error when titrating semicarbazide in the presence of semicarbazones.

On the basis of this study, the following procedure is employed in titrating semicarbazide with iodine. To 20 cc. of a 0.5 *M* phosphate buffer of P_H 7 (or, in the case of reactions taking place in acid solutions, the calculated amount of di-sodium phosphate to bring the P_H of the resulting solution to 7) enough 0.02 *M* iodine is added from a buret to provide a 2.5-cc. excess. A sample of the reacting solution is then added from a pipet and the excess of iodine is titrated back with thiosulfate.

Basicity of Semicarbazide.—The basicity of semicarbazide, expressed in terms of the acid dissociation constant K_A of the ion $H_2NCONHNH_3^+$, was determined at 24° (room temperature) and at 0° by potentiometric titration of semicarbazide hydrochloride with standard sodium hydroxide. The value of pK_A, the negative logarithm of K_A, was taken as equal to the P_H at the point of half neutralization on the curves shown in Fig. 1. The semicarbazide hydrochloride was tenth normal, and the ionic strength at the midpoint was 0.079. The values found for pK_A were 3.66 at 24° and 4.40 at 0°. Such values, of course, involve the magnitude of the activity coefficient of the semicarbazide positive ion (γ) and are therefore not the same at all ionic strengths. The quantity determined experimentally is

$$pK_A = P_H - \log \frac{(H_2NCONHNH_2)}{(H_2NCONHNH_3^+)} = pK - \log \gamma$$

If the approximate limiting equation held for the relation between γ and ionic strength at high dilutions

$$-\log \gamma = 0.5 \sqrt{\mu}$$

the value of $-\log \gamma$ at $\mu = 0.079$ would be 0.14, and the value of pK (infinite dilution) would be 3.52 at 24° and 4.26 at 0°. The experimentally determined values for pK_A were used in all the calculations, since semicarbazide was worked with in solutions of $\mu = 0.08$ and higher. pK_A at 25° was computed from its values at room temperature and 0° by applying the integrated form of the van't Hoff formula. This yields the value 3.68 for pK_A at 25° and $\mu = 0.079$.

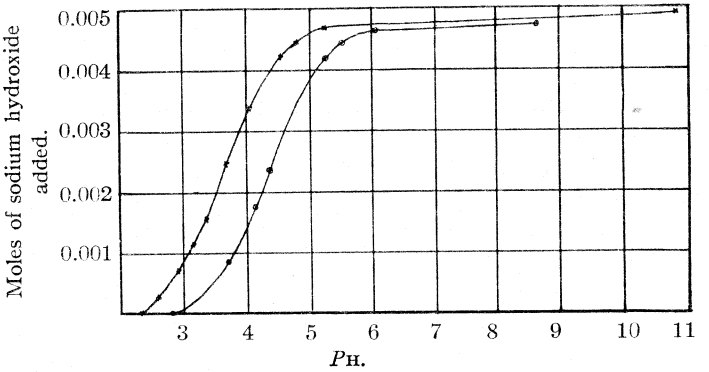


Fig. 1.—Titration of semicarbazide with sodium hydroxide: Crosses, 24°, Circles, 0°.

Two determinations of the basicity of semicarbazide are reported in the literature. Wood[4] reported K_B at 40.2° to be 2.6×10^{-11}, from studies of the hydrolysis of methyl acetate. Veley,[5] using methyl orange and a colorimeter, reported this constant to be 9.1×10^{-9} at 15°. The pK_A values corresponding to these are 2.90 and 6.25, respectively. Thus Wood's catalytic constant is in reasonable agreement with the present potentiometric results, while the work of Veley is not substantiated.

Experimental

The iodine–potassium iodide solution was standardized against weighed potassium bromate by comparing both with the thiosulfate solution on the same day. The iodine was 0.03365 *N*.

Semicarbazide hydrochloride from the Eastman Kodak Co. was recrystallized from alcohol–water. Its tenth normal solution was standardized by potentiometric titration with standard sodium hydroxide.

In the potentiometric titrations, a saturated calomel half-cell was used which had been standardized at the beginning of the run against a tenth normal calomel half-cell, whose single potential of 0.3377 volt at 24° was

[4] Wood, *J. Chem. Soc.*, **83**, 568–578 (1903).

[5] Veley, *ibid.*, **93**, 652–666 (1908).

in turn checked by measuring its e. m. f. against a $M/20$ solution of potassium hydrogen phthalate of assumed P_H 3.974.[6]

The buffer solutions were composed approximately as follows

P_H	Acid	Concentration	Salt	Concentration
1.48	H_3PO_4	0.295	Mono-sodium	0.205
2.02	H_3PO_4	.155	Mono-sodium	.345
2.45	H_3PO_4	.425	Mono-sodium	.075
3.01	Citric	.25	Mono-sodium	.25
3.57	Citric	.08	Mono-sodium	.42
5.01	Acetic	.17	Sodium	.33
7.08	NaH_2PO_4	.06	Di-sodium	.14

In measuring the rates of reaction at 25°, the following procedure was used. In each of a series of Erlenmeyer flasks were put 20 cc. of the appropriate buffer solution, 50 cc. of distilled water, and 5 cc. of a prepared iodine solution containing 2.18 cc. of the standard iodine. This was the amount calculated to react with 2.02 cc. of 0.00909 M semicarbazide hydrochloride, which was added to the flask from a pipet when the flasks had come to temperature in the thermostat. The several samples were thus identical and the excess iodine in the different flasks was titrated after suitable lengths of time. The time was measured to 0.01 minute with a stop watch.

In measuring the rate at 0° a similar procedure was used except that the total concentration of diluted reacting solution was in this case 100 cc., and the volumes of semicarbazide hydrochloride and of iodine solutions were, respectively, 2.02 and 2.39 cc. The reaction mixtures were kept in an ice-bath.

Summary

1. Semicarbazide reacts quantitatively, one molecule with four atoms of iodine.

2. The reaction is bimolecular; its rate is proportional to the non-ionized fraction of the semicarbazide up to P_H 5, but is considerably accelerated at P_H 7.

3. At P_H 7 the reaction is rapid enough to provide a suitable titration method for semicarbazide.

4. The basicity of semicarbazide has been determined by potentiometric titration at 0 and at 24°.

CAMBRIDGE, MASSACHUSETTS

[6] Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

THE BEHAVIOR OF ALIPHATIC DIAZO COMPOUNDS WITH DERIVATIVES OF METALS. I. MERCURI-ORGANIC DERIVATIVES AND MERCURIC SALTS WITH DIAZOMETHANE. (NOTE ON THE REACTION OF MERCURIC CHLORIDE WITH DIPHENYLDIAZOMETHANE)[1]

BY LESLIE HELLERMAN AND MINETTE D. NEWMAN

RECEIVED JANUARY 29, 1932 PUBLISHED JULY 6, 1932

Some years ago we were investigating the methylation with diazomethane of certain hydroxylated aromatic mercury derivatives,[2] as an aid to the elucidation of their structures. There was encountered, in the course of those studies, an interesting new reaction which seemed to involve essentially a transformation of the type represented by the equation

$$RHgX + CH_2N_2 \longrightarrow RHgCH_2X + N_2 \qquad (1)$$

The investigation of this reaction has recently been resumed by us and has included observations of the action of diazomethane and its derivatives upon a variety of simple mercuri-organic compounds and mercuric salts. Some of the results of the studies are recorded in this paper and certain theoretical implications set forth.

When *p*-tolylmercuric chloride, suspended in ether, is suitably treated with a molecular equivalent of diazomethane[3] a gas (nitrogen) is evolved and slightly soluble mercury di-*p*-tolyl remains suspended in the ether and may be separated from the latter by filtration; upon evaporation of the ether, there is obtained a third product, the hitherto unknown substance, bis-chloromethyl mercury.

$$2CH_3C_6H_4HgCl + 2CH_2N_2 \longrightarrow 2N_2 + (2CH_3C_6H_4HgCH_2Cl \longrightarrow) \\ CH_3C_6H_4HgC_6H_4CH_3 + ClCH_2HgCH_2Cl \qquad (2)$$

Thus diazomethane plays here the role of a peculiar type of "bridging" reagent which, itself, participates in the establishment of a new carbon-to-mercury bond. Its behavior, in this instance, bears a striking resemblance to its reactions[4] and those of some of its derivatives[5] with certain acid chlorides. Reference will be made to this further on. The assumption, implied in equation (2), that the unsymmetrical substance, chloromethyl *p*-tolyl mercury, is first formed and that this disproportionates to yield two

[1] This paper was presented before the Division of Organic Chemistry at the Buffalo Meeting of the American Chemical Society, September, 1930.

[2] Hellerman and Newman, unpublished work; Minette D. Newman, Doctorate Dissertation, The University of Chicago, 1930.

[3] See the Experimental Part for details.

[4] For references see Malkin and Nierenstein, THIS JOURNAL, **52**, 1504 (1930); Bradley and Robinson, *ibid.*, **52**, 1558 (1930).

[5] Staudinger and co-workers, *Ber.*, **49**, 1940, 1959, 1976 (1916).

symmetrical mercuri-bis compounds is supported by the work presently to be described. That this unsymmetrical derivative, if formed first, would very readily undergo disproportionation, seems to us entirely likely in view of the relatively great disparity in the apparent electron affinities of the groups carried by the mercury atom, that of the *p*-tolyl group presumably being high with respect to that of the chloromethyl group.[6]

From the interaction of phenylmercuric chloride and diazomethane there was obtained a liquid product ($C_6H_5HgCH_2Cl$?). After some time the product began slowly to deposit crystals of mercury diphenyl. This behavior suggested disproportionation, a change that would again be accompanied by the formation of bis-chloromethyl mercury.[7] The residual oil, separated from the precipitated mercury diphenyl, yielded, when treated with hot alcoholic hydrogen chloride, the beautifully crystalline new substance, chloromethylmercuric chloride, $ClCH_2HgCl$.

$$C_6H_5HgCH_2Cl + HCl \longrightarrow C_6H_6 + ClHgCH_2Cl \quad (3)$$

$$ClCH_2HgCH_2Cl + HCl \longrightarrow CH_3Cl + ClHgCH_2Cl \quad (4)$$

This was also obtained when bis-chloromethyl mercury, one of the products from the interaction of diazomethane and *p*-tolylmercuric chloride or mercuric chloride (equation 8), was similarly treated.[8]

These results encouraged us to attempt, by means of the interaction of diazomethane and a suitable mercury compound, the direct preparation of a relatively stable unsymmetrical derivative, disproportionation of which would take place but slowly. For this purpose, benzylmercuric chloride was selected, on the supposition that the desired stability in the product might be attained if the chloromethyl group were "balanced" against a group which, like itself, appears to possess relatively low electron affinity.[9]

[6] A large number of unsymmetrical mercury compounds, RHgR′, were prepared by Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926), by the use of the classical method whereby an organomagnesium halide is treated with an appropriate organomercuric halide. Careful control of the experimental conditions was found by them to be essential because of the tendency of these substances to undergo disproportionation. The results obtained from the decomposition of the unsymmetrical derivatives with alcoholic hydrogen chloride were used by these investigators in the construction of a table of organic groups in the order of their increasing "relative electronegativities" (apparent degrees of "affinity" or "attraction" of the organic groups for their assumed bonding electron pairs).

[7] Compare equation (2).

[8] Two reactions resulted when bis-chloromethyl mercury was treated with mercuric chloride: (1) the anticipated cleavage reaction in which the substance was converted to chloromethylmercuric chloride; and (2) an oxidation-reduction resulting in the formation of much *calomel*. For a discussion of the reactions of mercuri-bis compounds with mercuric halides consult Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Company, New York, 1921, p. 65.

[9] "Groups" that have *marked attractions* for their bonding doublet pairs (for example, C_6H_5 or Cl) often appear to induce a lowering of the *apparent* electron affinity of methyl carbon atoms upon which they are substituted. This principle cannot be

$$C_6H_5CH_2HgCl + CH_2N_2 \longrightarrow N_2 + C_6H_5CH_2HgCH_2Cl \quad (5)$$

As a matter of fact, benzyl chloromethyl mercury, the liquid product (obtained in practically quantitative yield) from the action of diazomethane upon benzylmercuric chloride, showed little apparent tendency to disproportionate while standing for a period of several weeks. The identity of the product was demonstrated by means of (a) analysis, (b) evidence of homogeneity after an attempted fractionation with ether, and (c) its behavior during decomposition with hydrogen chloride on the one hand and mercuric chloride on the other.

It seems worthy of emphasis that a completely unsymmetrical breakdown in benzyl chloromethyl mercury resulted from the action upon it of alcoholic hydrogen chloride. The only mercury compound produced as a result of this process was chloromethylmercuric chloride. This was obtained directly in a high state of purity and in good yield. In the reaction mixtures from several independent experiments benzylmercuric chloride was sought but could not be detected. The change may, therefore, be represented by the following equation.[10]

$$C_6H_5CH_2HgCH_2Cl + HCl \longrightarrow C_6H_5CH_3 + ClHgCH_2Cl \quad (6)$$

Of especial interest in connection with the foregoing are the reactions of mercuric salts with aliphatic diazo compounds. It had already been incidentally observed[11] that diazomethane *reduces* mercuric chloride. However, employment of the experimental procedure developed in this work has demonstrated that the course of the reaction may be very different. From mercuric chloride with one molecular equivalent of diazomethane, there was obtained in high yield chloromethylmercuric chloride.

$$ClHgCl + CH_2N_2 \longrightarrow N_2 + ClCH_2HgCl \quad (7)$$

The same salt with two equivalents of the diazo compound yielded the expected symmetrical derivative, bis-chloromethyl mercury.

$$ClHgCl + 2CH_2N_2 \longrightarrow 2N_2 + ClCH_2HgCH_2Cl \quad (8)$$

It has already been stated that chloromethylmercuric chloride is obtained as a product when bis-chloromethyl mercury is decomposed by either hydrogen chloride or mercuric chloride. Both compounds are physiologically active; for example, in minute quantities they act upon the skin causing a "dermatitis." This may be severe in the case of individuals who are very susceptible to the action of mercurials. The di-chloromethyl compound is a powerful vesicating agent and causes painful blisters.

elaborated here. It is illustrated by certain aspects of the chemical behavior of such compounds as benzyl-, benzohydryl- and triphenylmethylmagnesium halides, highly phenylated hydrocarbons, phenylated or halogenated acetic acids, etc.

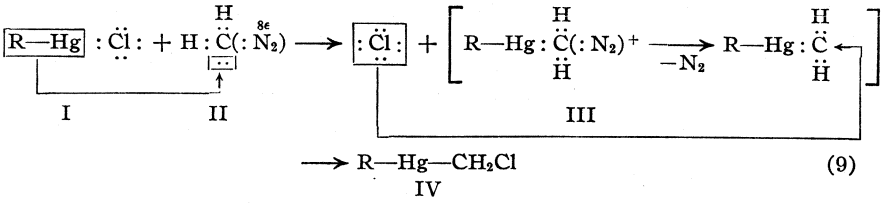
[10] When mercuric chloride was substituted for hydrogen chloride in this reaction, there was produced the expected *mixture* of chlorides. On the basis of the result of the hydrogen chloride reaction it would be concluded, following Kharasch's reasoning (see Ref. 6), that the group, $ClCH_2$—, is less "electronegative" than the benzyl group.

[11] Meerwein and Burneleit, *Ber.*, **61B**, 1843 (1928).

In contrast to the chloride, mercuric iodide does not react "smoothly" with diazomethane. With either one or two molecular equivalents of the diazo compound, mercuric iodide yields but a small amount of a pure crystalline product that is probably bis-iodomethyl mercury, $(ICH_2)_2Hg$. A large proportion of gummy material, that has not yet been carefully examined, is formed at the same time. This difference in behavior may be related to the fact that the tendency toward the formation of complex salts seems to be more pronounced in the case of mercuric iodide than mercuric chloride. Under the experimental conditions diazomethane may in effect be acting upon the simple salt, HgI_2, in the presence of "complexes," $(HgI_2)_n$.[12]

Diazomethane reacts also with mercuric acetate and with "bases" such as phenylmercuric hydroxide.[13] These reactions involve some novel features and require further study. Toward mercury diphenyl,[14] mercury di-*p*-tolyl and mercuric cyanide the diazo compound is not active under the experimental conditions used. The aliphatic diazo compounds react with certain salts and organic derivatives of metals other than mercury. This general behavior is now under investigation in this Laboratory, since it appears to hold a considerable interest from the theoretical as well as the synthetic point of view.

It has been found useful to interpret the reaction type described in this paper in terms of an "electronic" formula for diazomethane and its derivatives. The mechanism is schematically represented as follows.



The formula (II) is essentially that proposed by Professor W. A. Noyes for diazomethane, except that eight valence electrons (8ε) are assigned to the diazo group as a whole since their exact distribution is not certain.[15] The "driving force" of the reaction is considered to be related to the ultimate "sharing" of an electron pair of the diazo carbon atom with the relatively oxidized mercuric atom. The diazonium ion (III) might thus transi-

[12] Compare Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); *ibid.*, **39**, 485 (1881).

[13] Compare Buchner, *Ber.*, **28**, 218 (1895).

[14] Mercury diphenyl, after treatment with diazomethane in ether solution, was recovered unchanged.

[15] This formula is used here as a *convenience* to depict a potentially reactive form of diazomethane. The enclosed electron pair (|:·:|) is considered to be only potentially "exposed" as represented. The matter will be more fully discussed in a forthcoming communication by the senior author and R. L. Garner. See also Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1722 (1928), footnote 25.

torily exist; but the concomitant destruction of the electrical neutrality of the diazo molecule would cause the diazo group to be "lost" together with the electron pair with which it is bound to the carbon atom (*i. e.*, as N_2) and the latter would again complete its octet by attracting Cl^- with the elaboration of the final product (IV).

An analogous interpretation for the reactions of acid chlorides[4,5] with diazo compounds should be of service. Here the carboxyl carbon atom is the *relatively* oxidized atom that would "share" an electron pair with the diazo carbon atom in the first stage of the reaction. Such reactions seem to be closely allied to the changes involved in the decomposition of diazo compounds with acids, in which hydrogen ions presumably share the "exposed" doublet pairs.

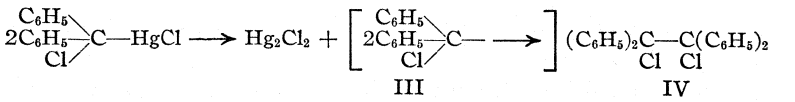
Staudinger has demonstrated that chloro-ketonic derivatives may be formed when certain acid chlorides react with aliphatic diazo compounds in which the diazo carbon atoms are *fully substituted* (*i. e.*, carry no hydrogen atoms). In the following section preliminary results are presented that indicate that a diazo compound of that type may also react with mercuric chloride. The applicability of the concept of "electron-sharing" as tentatively suggested in the foregoing is thus strengthened.

Mercuric Chloride with Diphenyldiazomethane.—When mercuric chloride is treated with diphenyldiazomethane (I), under the conditions used, nitrogen is evolved and there is obtained, as the main product, a white amorphous solid which is not appreciably soluble in dry ether. This solid has the mercury content calculated for chlorodiphenylmethylmercuric chloride (II).

$$\underset{\text{I}}{HgCl_2 + (C_6H_5)_2C(N_2)} \longrightarrow N_2 + \underset{\text{II}}{\begin{matrix} C_6H_5 \\ C_6H_5 \\ Cl \end{matrix}\!\!>\!C\!-\!HgCl} \qquad (10)$$

Upon exposure to moist air, it is converted chiefly to benzophenone and calomel. Hydrogen chloride is also formed. Of preëminent interest is its behavior when shaken with moist ether. Calomel is produced *quantitatively* and, at the same time, organic material dissolves in the ether, which is abruptly colored yellow. This indicates cleavage at the carbon-to-mercury bond, a property to be anticipated for a substance of the type assumed.[16] From the ethereal solution, after spontaneous evaporation of the solvent (during which the yellow color vanishes), there is obtained chiefly a white crystalline substance. The properties of the latter indicate that it is 1,2-dichlorotetraphenylethane. The following equation depicts the assumed course of the decomposition.

[16] Triphenylmethylmercuric bromide, $(C_6H_5)_3CHgBr$, would be a similar substance of much theoretical interest. It is not produced when triphenylmethylmagnesium bromide is treated with mercuric bromide. Instead, the mercuric salt is reduced; triphenylmethyl bromide is a product of the reaction (unpublished results of the authors).



(11)

Work is being continued upon the preparation and properties of unstable metallic derivatives of this type (II) and upon the probable elaboration from them of free radicals (III). Enough has been accomplished here to indicate that the new reaction type considered in this paper is applicable also to *derivatives* of diazomethane and that the mechanism suggested [equation (9)] for the course of such reactions is not inconsistent with the experimental results.

Experimental Part

For the addition of diazomethane to the various mercury compounds treated, a simple standard type of apparatus was found useful. The reaction vessel, set up in a good hood, was a three-necked flask of convenient volume fitted with (a) a short return condenser ("closed" with a calcium chloride tube), (b) a mercury-sealed stirrer and (c) the delivery end of a condenser which in turn was sealed to the outlet tube of a suitable distilling flask to be used for the generation of diazomethane. The distilling flask was equipped with a dropping funnel.

The Interaction of Mercuric Chloride and Diazomethane in Equimolecular Proportions: Chloromethylmercuric Chloride, $ClCH_2HgCl$.—Pure mercuric chloride, 13.6 g. (0.05 mole), and 200 cc. of ether (C. P.) were mixed in the reaction flask which was placed in an ice-bath. The mixture was well stirred mechanically. In the distilling flask a molecular equivalent (2.1 g.) of diazomethane[17] was prepared in the usual manner by the slow addition of 12.0 cc. of nitrosomethylurethan to a mixture of 60 cc. of ether and 18 cc. of a 25% solution of potassium hydroxide in methyl alcohol. The ethereal diazomethane was distilled during its preparation directly into the reaction vessel at such a rate that the mercuric chloride was always in excess and the reaction mixture remained colorless. The reaction took place rapidly with the evolution of nitrogen. At the end of the operation the product had crystallized partially. It was obtained in almost pure form and in practically quantitative yield after the solvent had been allowed to evaporate spontaneously. Recrystallization of the product from 95% ethanol yielded micaceous scales of the pure substance; m. p. 131° (corr.). The substance is slightly soluble in water. It is appreciably hydrolyzed in its aqueous solution. It is decomposed in the presence of concentrated sodium hydroxide with the formation of metallic mercury.

Anal. Subs., 0.2776 g.: required 16.25 cc. of NH_4CNS (1.00 cc. = 0.01196 g. Hg). Calcd. for CH_2Cl_2Hg: Hg, 70.3. Found: Hg, 70.0. Subs., 0.4287, 0.4945 g.: AgCl, 0.4384, 0.4976. Calcd. for CH_2Cl_2Hg: Cl, 24.8. Found: Cl, 25.3, 24.9.

Analytical Methods. (1) Mercury.—The convenient thiocyanate method gave excellent results when used in conjunction with the treatment (somewhat modified) recommended by Kharasch and Flenner (cited by Hillebrand and Lundell)[18] for mercury compounds containing halogens.

(2) Halogens.—In a long-necked flask fitted with a condenser (preferably with a ground-glass seal) the substance, suspended in anhydrous ethanol, is decomposed by

[17] The directions given in Houben–Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1923, Vol. III, p. 124, were found reliable; it was considered that 1 cc. of ethyl-N-methyl-N-nitrosocarbamate (nitrosomethylurethan) produced 0.18 g. of diazomethane.

[18] Hillebrand and Lundell, "Applied Inorganic Analysis," Wiley, New York, 1929.

the addition of pieces of pure sodium. Water is then added and the alcohol removed by distillation. The residual solution is filtered and neutralized with nitric acid. Halogen is determined in the usual manner.

Mercuric Chloride with Diazomethane in Excess: Bis-Chloromethyl Mercury, $(ClCH_2)_2Hg$.—In the standard apparatus and under conditions of temperature, stirring, etc., identical with those set forth in the preceding section, mercuric chloride in ethereal solution and suspension was treated with two molecular equivalents and a 10% excess of diazomethane. At the end of the operation, the solution of the product was colored yellow (excess diazomethane). It was filtered from a trace of calomel and the filtrate evaporated as completely as possible in a rapid stream of calcium chloride-dried air. A slightly colored oil remained; its weight was that expected, assuming that bis-chloromethyl mercury had been formed quantitatively. The crude product was assayed (calcd.: Hg, 67.0. Found: Hg, 63.6, 63.4). After several days the oil crystallized, when manipulated; the crystals consisted of rods and plates. Although they were quite soluble in various organic solvents, it was found possible to effect the purification of a quantity sufficient for analysis by means of recrystallization from ether. A second recrystallization from isopropyl ether yielded material with the same melting point. The latter property was evidently materially affected by the presence of small amounts of impurities; m. p. 37–40° (rather indefinite). The molten substance re-solidified upon cooling. The physiological properties are touched upon in the first part of the paper.

Anal. Calcd. for $C_2H_4Cl_2Hg$: Hg, 66.98. Found: Hg, 66.83, 66.97.

Bis-Chloromethyl Mercury with Mercuric Chloride.—Of the bridged compound, 2 g. was heated with a mixture of 15 cc. of ethanol and 2 g. of mercuric chloride just below the boiling point of the solvent for one-half hour. The compound dissolved; a solid product precipitated. The mixture was filtered while hot. The residue consisted of 0.91 g. of calomel, which was identified by its physical and chemical properties. When the filtrate was cooled there were obtained characteristic spangles of chloromethylmercuric chloride. The product was pure; it melted at 128° (uncorr.) and did not depress the melting point of known chloromethylmercuric chloride.

Bis-Chloromethyl Mercury with Hydrogen Chloride.—Some of the substance was heated for ten minutes with a freshly prepared, concentrated solution of hydrogen chloride in ethanol at the boiling point of the solvent. Crystals did not appear until the reaction mixture had been permitted to stand at room temperature for a week. After most of the solvent had evaporated spontaneously, the characteristic scales that had been formed were collected and washed with alcohol. They were in all respects identical with chloromethylmercuric chloride; m. p. 129° and "mixed m. p." 129°. This was the only mercury compound that could be isolated from the reaction mixture.

$$ClCH_2HgCH_2Cl + HCl \longrightarrow CH_3Cl + ClCH_2HgCl \qquad (12)$$

The Interaction of Diazomethane and *p*-Tolylmercuric Chloride.—*p*-Tolylmercuric chloride, 16.4 g. (0.05 mole), suspended in 100 cc. of pure ether, was treated at 0° with 2.4 g. of diazomethane (0.055 mole) in a manner entirely similar to that described in the foregoing except that the ethereal diazomethane was added rather rapidly. There was no difficulty in controlling the action, which was slow but increased in rate when the temperature was raised somewhat. After the evolution of nitrogen had entirely ceased (two hours) the suspended solid was collected on a filter and washed *well* with ether. The product contained no chlorine; it was identified as mercury di-*p*-tolyl (7.1 g.) by its solubility behavior and its melting point (233–236°). It depressed the melting point of a sample of *p*-tolylmercuric chloride and did not depress that of authentic mercury di-*p*-tolyl ("mixed m. p." 236°).

The ether filtrate from the solid product was evaporated in a stream of dry air. A slightly colored viscous oil remained which resembled in appearance and properties

crude *bis*-chloromethyl mercury. Possibly some chloromethyl *p*-tolyl mercury was present. The oil was treated with concentrated alcoholic hydrogen chloride according to the directions of the preceding section. The results of this experiment were analogous to those noted for the corresponding decomposition of known bis-chloromethyl mercury. But one substance containing mercury was isolated. The product, obtained in excellent yield, was identical in all respects with samples of chloromethylmercuric chloride which had been prepared during the course of this investigation from other sources. It melted at 131° (corr.). For analysis it was recrystallized from ethanol and dried over phosphoric anhydride and paraffin.

Anal. Calcd. for CH_2Cl_2Hg: Hg, 70.3. Found: Hg, 69.7, 70.2.

The Interaction of Diazomethane and Phenylmercuric Chloride.—Phenylmercuric chloride was treated with diazomethane according to the general procedure. During the action, the evolution of gas proceeded evenly and the mercurial gradually "dissolved"; the action ceased abruptly and the reaction mixture became yellow immediately after one molecular equivalent of the diazo compound had been added. The solution thus obtained was cooled (5°) and concentrated in a stream of dry air. A colorless oil remained. Upon standing some needle-like crystals were deposited from the oil and the amount soon became very appreciable. Those were collected and washed with ether; they were found to be slightly impure mercury diphenyl. They were identified (a) by means of comparison with authentic mercury diphenyl and (b) by the observation that their decomposition in the presence of alcoholic mercuric chloride yielded only pure phenylmercuric chloride (m. p. 252°, "mixed m. p." 252°).

The residual oil (filtrate from the mercury diphenyl) was mixed with alcoholic hydrogen chloride and the mixture heated for fifteen minutes. When the mixture was cooled there crystallized pure chloromethylmercuric chloride, identified by comparison with authentic material (see above).

The Interaction of Diazomethane and Benzylmercuric Chloride: Benzyl Chloromethyl Mercury, $C_6H_5CH_2HgCH_2Cl$.—Benzylmercuric chloride, 8.18 g., was suspended in 200 cc. of ether (c. P.). To the mixture, cooled to 0° and stirred well, was added 1.05 g. of diazomethane (a 5% excess) in ether solution. The general procedure, as described in preceding experiments, was employed. The reaction proceeded slowly with the evolution of nitrogen; the gas ceased to be evolved after one equivalent of the diazo compound had been added and at this stage all of the suspended solid had "dissolved." Ether and excess diazomethane were next removed in a blast of clean, dry air and an oil, colored faintly yellow, remained. Crystallization of the product could not be effected. The initial unpleasant odor of the product vanished after the oil had been brought to constant weight (at room temperature) in a vacuum desiccator (over chipped paraffin and phosphoric anhydride). The yield of the product was quantitative. Its analysis indicated that it was either an equimolecular mixture of mercury dibenzyl and mercury di-chloromethyl or the unsymmetrical compound, benzyl chloromethyl mercury. That the latter alternative is correct was rather convincingly demonstrated by the experiments to be described.

Anal. Calcd. for C_8H_9ClHg: Hg, 58.8. Found: Hg, 58.4, 58.8.

Decomposition with Hydrogen Chloride.—Benzyl chloromethyl mercury, 22.4 g., was treated with 125 cc. of alcoholic hydrogen chloride on a water-bath for fifteen minutes. The odor of toluene became evident almost at once. To the solution, which had been freed from a suspended trace of mercury by means of filtration, was added water; a large amount of solid was precipitated. The solid was collected and directly (without being washed) dried in a vacuum desiccator over paraffin and phosphoric anhydride. It consisted of 14.8 g. of practically pure chloromethylmercuric chloride (m. p. 129–131°; m. p. of a mixture with authentic material, 129–131°). The filtrate

contained more of the same substance. The product was recrystallized from ethanol; m. p., unchanged. No other mercury compound could be isolated from the reaction mixture. The decomposition of benzyl chloromethyl mercury by hydrogen chloride took thus the course depicted by equation (6).

Decomposition with Mercuric Chloride.—The decomposition of benzyl chloromethyl mercury with hot alcoholic mercuric chloride resulted in the production of a substantial amount of calomel together with a mixture of benzylmercuric chloride and chloromethylmercuric chloride. The nature of the mixture was indicated by its melting point behavior before and after a partial fractionation with alcohol; the products were compared with the pure individual chlorides.

An Attempt at Fractionation.—Some benzyl chloromethyl mercury (about 8 g.) was well agitated with a little ether until about one-third had dissolved. The extract was separated from residual oil (R) by decantation and the two fractions freed from ether and brought to constant weight in the manner already described. The two fractions were found to be identical in their chemical behavior (decomposition reactions, etc.); their mercury contents were identical.

Anal. Calcd. for C_8H_9ClHg: Hg, 58.8. Found: (first fraction, R) Hg, 58.6; (second fraction) Hg, 58.6.

It had been observed that occasionally freshly prepared benzyl chloromethyl mercury contained in suspension a trace of mercury, from which it could be separated by filtration. As the unsymmetrical compound stood the formation of mercury continued; heat or exposure to light accelerated the process. The nature of this oxidation–reduction change was not studied in detail; such behavior is not unusual for compounds of this type. The fractions described above were permitted to stand for several weeks, after which they were separated from precipitated mercury. They were then assayed for chlorine and, as was expected, the chlorine contents were somewhat high.

Anal. Calcd. for C_8H_9ClHg: Cl, 10.4. Found: (first fraction, R) Cl, 11.0; (second fraction) Cl, 10.8.

Diazomethane and Mercuric Iodide: Bis-iodomethyl Mercury, $(ICH_2)_2Hg$(?).—Of red mercuric iodide (C. P.), one-twentieth mole was treated with one-tenth mole of diazomethane, the procedure being entirely similar to the general method already described. A vigorous action ensued and nitrogen was evolved. However, much solid remained undissolved. Some of it was probably yellow mercuric iodide. When the action had ceased, the ether solution was still deeply colored (yellow diazomethane). The solution was separated from undissolved yellowish material (S) and the removal of ether and diazomethane effected as usual. During the evaporation, some well-formed long needles crystallized; m. p. 80–84°. The solid (S) possessed a disagreeable odor; when heated with various alcohols or ethers it became gummy and but little dissolved in the solvents. Nevertheless, some indefinite crystalline matter precipitated when methyl alcohol, ether or isopropyl ether extracts were cooled. After repeated recrystallizations of this from isopropyl ether, there was obtained a pure substance as fine, white, silky plates; m. p. 82–84°. The total yield amounted to but a few grams. In another preparation in which mercuric iodide was treated with one molecular equivalent of diazomethane, diazomethane again remained in excess and the final results were similar to those described, except that less of the pure product was obtained.

Anal. Calcd. for $C_2H_4I_2Hg$: Hg, 41.6. Found: Hg, 41.6, 41.7.

Diazomethane with Mercuric Cyanide.—Of powdered mercuric cyanide, 6.32 g. (one-fortieth mole) suspended in ether was treated with diazomethane (one-fortieth mole). No action took place, although the mixture was finally boiled (refluxed) for some time. There was recovered 6.20 g. of the mercuric salt.

Diphenyldiazomethane and Mercuric Chloride.—To pure, dry mercuric chloride, one-twentieth mole, in 150 cc. of anhydrous ether, cooled to 0° and stirred mechanically, was added during one hour a molecular equivalent of diphenyldiazomethane[19] (dissolved in a little ether). Care was taken to exclude moisture. The pink color of the diazo compound vanished, a gas was evolved and a pale yellow product, insoluble in the ether, appeared. The product was rapidly brought upon a Buchner funnel, washed thoroughly with anhydrous ether and dried at room temperature for twelve hours in a vacuum over phosphoric anhydride and chipped paraffin. When the preparation was carried out as described, the ether filtrates contained but little dissolved material. An analysis indicated that the product might be chlorodiphenylmethylmercuric chloride, $Cl(C_6H_5)_2C \cdot HgCl$.

Anal. Calcd. for $C_{13}H_{10}HgCl_2$: Hg, 46.9. Found: Hg, 47.5.

When some of the product was exposed to moist air, it was hydrolyzed and decomposed rather rapidly with the evolution of hydrogen chloride. All of the mercury in the initial compound was recovered as *calomel*, insoluble in ether, when the decomposed material was extracted with that solvent. When the ether was allowed to evaporate spontaneously there remained a colorless oil that crystallized in prismatic plates when "seeded" with benzophenone. That the material was chiefly benzophenone was indicated by its melting point and conversion to benzophenone oxime. Air oxidation was probably a factor here; further data are required for an accurate description of the nature of the change. Calomel is also one of the products when the compound is decomposed thermally in the presence of xylene.

Some of the supposed chlorodiphenylmethylmercuric chloride was covered with anhydrous ether. When a drop of water was added and the mixture shaken, the ether became *pronouncedly yellow* and a white solid remained undissolved. That the latter was calomel was proved by its properties (ammonia test, etc.) and an assay of its mercury content. The formation of calomel was shown to be quantitative. Samples were decomposed as described; the residues of calomel were collected in Gooch crucibles, washed well with ether, alcohol and water and dried to constant weight over phosphorus pentoxide.

Anal. Subs., 0.2994, 0.2978: Hg_2Cl_2, 0.1656, 0.1635. Calcd. for $C_{13}H_{10}Cl(HgCl)$: (HgCl), 55.2. Found: (HgCl), 55.3, 54.9.

From the yellow ether filtrates (from the calomel) the solvent was permitted to evaporate spontaneously. The residue consisted of a portion very soluble in ether and a less soluble part. The former portion contained benzophenone. The less ether-soluble material consisted of large, white, thick, rhomboidal plates. These were purified by means of crystallization and recrystallization from a mixture of benzene and isopropyl ether (1:3). They melted and decomposed at 183° with the evolution of hydrogen chloride. The physical and chemical properties of this product and its analysis indicated that it was 1,2-dichlorotetraphenylethane.[20]

Anal. Subs., 0.2449: CO_2, 0.6943; H_2O, 0.1092. Calcd. for $C_{26}H_{20}Cl_2$: C, 77.4; H, 4.96. Found: C, 77.3; H, 4.98.

Summary

1. It is shown that, under appropriate conditions, diazomethane reacts with a variety of mercuric salts and mercuri-organic derivatives with the formation of interesting new products. For example, from mercuric chloride, mercuric iodide and benzylmercuric chloride there are obtained, respectively, bis-chloromethyl mercury (and chloromethylmercuric chlo-

[19] Staudinger, Anthes and Pfenninger, *Ber.*, **49**, 1932 (1916).

[20] Schmidlin and Escher, *ibid.*, **43**, 1153 (1910).

ride), bis-iodomethyl mercury and benzyl chloromethyl mercury. The primary product of the interaction of diazomethane and *p*-tolylmercuric chloride undergoes disproportionation, yielding mercury di-*p*-tolyl and bis-chloromethyl mercury; that from phenylmercuric chloride behaves analogously.

2. There are described the reactions with alcoholic hydrogen chloride and those with mercuric chloride of bridged mercury compounds prepared in this work. With the former reagent benzyl chloromethyl mercury yields toluene and chloromethylmercuric chloride and no benzylmercuric chloride.

3. Aliphatic diazo compounds react also with some other types of mercury compounds and with certain salts and organic derivatives of metals other than mercury. Mercuric chloride and *diphenyldiazomethane* interact forming, apparently, diphenylchloromethylmercuric chloride. The latter displays interesting decomposition reactions.

4. Certain theoretical implications of the results of the investigation are discussed.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

AN OPTICAL METHOD FOR THE STUDY OF REVERSIBLE ORGANIC OXIDATION–REDUCTION SYSTEMS. I. PARA-BENZOQUINONES[1]

BY W. H. HUNTER AND D. E. KVALNES

RECEIVED FEBRUARY 5, 1932 PUBLISHED JULY 6, 1932

Introduction

Extensive studies have been made on the reduction potentials of reversible organic oxidation–reduction systems.[2] In one of these investigations, Conant and Fieser[2h,k] determined the oxidation–reduction potentials of a number of systems composed of a quinone and its hydroquinone referred to the solid, dissolved and gaseous states.

[1] (a) The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Donovan E. Kvalnes in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931. This paper was prepared by the junior author after the death of Dr. W. H. Hunter.—L. I. Smith. (b) Presented at the spring meeting of the American Chemical Society, New Orleans, 1932.

[2] (a) Granger and Nelson, THIS JOURNAL, **43**, 1401 (1921); (b) Clark, *J. Wash. Acad. Sci.*, **10**, 225 (1920); (c) Clark, *Science*, **54**, 557 (1921); (d) Biilmann, *Ann. chim.*, **15**, 109 (1921); (e) Conant, Kohn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922); (f) La Mer and Baker, *ibid.*, **44**, 1954 (1922); (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922); (h) Conant and Fieser, *ibid.*, **45**, 2194 (1923); (i) Biilmann, *Trans. Faraday Soc.*, 676 (1923); (j) Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924); (k) Conant, *ibid.*, **49**, 293 (1927); (l) Fieser, *ibid.*, **51**, 3101 (1929).

They found that in general the order of the potentials is alcoholic solution > aqueous solution > solid state > gaseous state; that the introduction of methyl groups progressively and regularly decreases the potentials; that in all but the gaseous state the introduction of chlorine into the quinone first raises and then lowers the potential.

In a few cases the potentials of the corresponding chloro and bromo quinones have been determined.[2f,g,i] These results, together with the data of Conant and Fieser[2j] on derivatives of naphtho and anthraquinones and the data of Clark[3] on oxidation–reduction indicators show that the effect of the introduction of chlorine and bromine is identical within the limits of the significance of the data.

Since the potential of a quinone–hydroquinone combination depends upon the state of the system, *i. e.*, whether solid, dissolved or gaseous, the question arises as to which is the preferred state in which to study the result of substitution of the parent compound. Conant[2k] believes that the gaseous state is the one to be selected, with a dilute solution as second choice, in order to eliminate secondary effects such as solubilities or the affinity of the quinone and hydroquinone molecules for each other.

Since there is no general agreement among the potentials of a series of quinones, determined in different states, and since potential measurements have been used as evidence in problems of chemical constitution, it seemed advisable to attack this question of oxidizing strength by some method other than an electrochemical one. This has been accomplished in the following manner.

If one mole of a hydroquinone (H_2Q) is in solution with one mole of some quinone (Q'), an equilibrium will eventually result, as shown by the equation

$$H_2Q + Q' \rightleftharpoons H_2Q' + Q$$

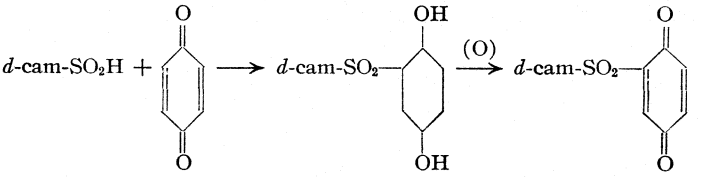
The same equilibrium may be reached by starting with one mole each of Q and H_2Q'. If the H_2Q–Q pair were an optically active hydroquinone and quinone, it would be possible to measure the concentration of each substance involved in the equilibrium. This would afford a means of grading the oxidizing strength of a series of hydroquinone–quinone pairs, represented by H_2Q'–Q', against a given optically active pair, H_2Q^*–Q^*, used as a standard. If the H_2Q'–Q' pair were a stronger oxidizing agent than the standard pair, and if a mole each of H_2Q^* and Q' were used at the start, then at equilibrium there would be proportionately more Q^* present than H_2Q^*. The reverse would be true if the Q'–H_2Q' pair were a weaker oxidizing agent than the standard pair.

By this method of determining the concentrations, the equilibrium can in no way be affected. However, for accurate measurements it would be necessary to employ an optically active quinone and hydroquinone with a

[3] Clark, *Chem. Reviews*, **2**, 127 (1925).

relatively large difference in specific rotations, since the actual rotation would be a summation of the rotations due to each in the equilibrium mixture. A search of the literature failed to show any optically active compounds fulfilling these requirements and, therefore, the first part of this work dealt with the preparation of a series of such compounds.[4]

Optically Active Quinones and Hydroquinones.—The optically active hydroquinones were prepared by treating a quinone with *d*-camphorsulfinic acid, to give the *d*-camphorsulfone of the hydroquinone, according to the method of O. Hinsberg.[5] A few of the corresponding optically active quinones were made by oxidation of the respective hydroquinones.



The specific rotations of the hydroquinones are given in Table I.

TABLE I

ROTATIONS OF OPTICALLY ACTIVE HYDROQUINONES

d-Camphorsulfone of	$[\alpha]^{27}_{5461}$ in benzene
Hydroquinone	+46.5°
2,6-Dibromohydroquinone	37.9
2,6-Dichlorohydroquinone	35.4
2,5-Dibromohydroquinone	19.6
2,5-Dichlorohydroquinone	29.9
2,5-Dimethylhydroquinone	24.2

With regard to this table, it will be noted that the unsubstituted hydroquinone has the highest rotation, while the introduction of methyl groups or halogen atoms causes a lowering of the rotation. The position of substitution is of importance since the 2,6-dihalogen derivatives have higher rotations than have the corresponding 2,5-dihalogen compounds. This is much more marked in the case of the bromo than in the chloro compound.

The rotations of the quinones are given in Table II.

TABLE II

ROTATIONS OF OPTICALLY ACTIVE QUINONES

d-Camphor sulfone of	$[\alpha]^{27}_{5461}$ in benzene
Benzoquinone	+305.5
α-Naphthoquinone	237
p-Xyloquinone	223

[4] While this research was in progress, a paper by Hill and Adams [THIS JOURNAL **53**, 3453 (1931)] appeared, in which an optically active quinone was prepared and resolved, although the corresponding hydroquinone was not resolved.

[5] Hinsberg, *Ber.*, **27**, 3259 (1894); *ibid.*, **28**, 1315 (1895); *ibid.*, **29**, 2025 (1896).

The unsubstituted quinone has the highest rotation. Two methyl groups, in the 2,5-positions, have a greater lowering effect than a condensed ring. The rotations of the quinones are much greater than those of the corresponding hydroquinones. This would be expected due to the change of the benzenoid to the quinoid structure, since unsaturation has a marked effect on rotations.

Choice of a Standard.—The hydroquinone–quinone pair chosen as a standard was the *d*-camphorsulfone of 2,5-dimethylhydroquinone and the corresponding quinone. These two compounds are fairly easy to obtain in a pure condition and have a large difference in specific rotations. Benzene was selected as a solvent because it is a non-polar liquid and, therefore, larger specific rotations are secured.[6]

Soon after the addition of a quinone to the H_2Q^*, there are present in the solution two hydroquinones and two quinones

$$H_2Q^* + Q' \rightleftharpoons Q^* + H_2Q'$$

Furthermore, there is the possibility of the formation of the following four quinhydrones: (H_2Q^*–Q'), (H_2Q^*–Q^*), (H_2Q'–Q'), (H_2Q'–Q^*). If one of these is formed more readily than the others, the point of equilibrium will not be the same as it would if there were no quinhydrones present. However, it is impossible to determine the exact amounts or the specific rotations of the quinhydrones.

It is not possible to measure the effect of an optically inactive quinone on the rotation of the optically active hydroquinone, and *vice versa*, because of immediate oxidation and reduction to form new compounds according to the equation above. However, by adding definite amounts of the H_2Q^* to the Q^* and determining the resulting rotation, it is possible to ascertain whether or not there is any effect on the individual rotations of the two compounds due to association or quinhydrone formation. If the resultant rotation is the sum of the individual rotations, observed under the same conditions, then no association has occurred.

Twenty-five cc. of benzene containing 0.0855 g. of H_2Q^* and 0.0850 g. of Q^* gave 98.8% of the calculated rotation, and gave 100% of the calculated value when diluted to 50 cc. Accordingly, subsequent measurements were carried out with solutions sufficiently dilute to obviate association.

General Procedure

A weighed amount of a given quinone was added to a weighed sample of H_2Q^*. Enough benzene was added to dissolve the two compounds and the solution was allowed to stand for several hours. It was then diluted to a definite volume and the rotation was determined. Rotations were again observed after various periods of time. The rotation of the solution rose slowly to a definite value, remained constant at this point for several hours

[6] Rule and McLean, *J. Chem. Soc.*, 674 (1931).

to a day and then dropped, often quite abruptly. The equilibria were established after lengths of time varying from a few hours to two days. Several determinations were carried out at different concentrations, and the equilibrium constants thus calculated served to check the separate runs.

Because the equilibrium points are not rapidly reached, it was necessary to determine whether or not the rotations of the optically active compounds change with time. The optically active hydroquinone showed no change in rotation even after several days. However, the rotation of the optically active quinone dropped slowly during the same period of time. Although this introduces an error into the determinations, it is a small one. Moreover, since the observed equilibrium points, using various quinones, are reached in approximately the same length of time, this error does not affect the comparative results.

Calculation of Conversions.—If a quinone Q′ be added to H_2Q^*, in equimolecular amounts, the following equilibrium will be reached

$$H_2Q^* + Q' \rightleftharpoons Q^* + H_2Q'$$

If the concentrations of H_2Q^* and Q′, at the start, be represented by 1, and the concentrations of Q^* and H_2Q' at equilibrium be represented by β, then the concentrations of H_2Q^* and Q′ at equilibrium will each be $(1-\beta)$. The equilibrium constant for the reaction is given by the equation $K = \beta^2/(1-\beta)^2$. To calculate β it is necessary to know the actual rotation of H_2Q^* at the start (A), the actual rotation of Q^*, if all the H_2Q^* were changed to Q^*, (B), and the observed rotation (C). These values must be calculated for definite concentrations in a given solvent. At equilibrium, the contribution of H_2Q^* to the observed rotation will be $A(1-\beta)$ and the contribution of Q^* will be $B\beta$. The observed value for the rotation of the solution (C) will be the sum of the above two values. $C = A(1-\beta) + B\beta$; from which $\beta = (C - A)/(B - A)$. β will be a measure of the oxidizing strength of the system H_2Q' and Q′ referred to the standard system, H_2Q^* and Q^*, in the solvent used. The conversion β_0 of any quinone Q′, will be defined as the percentage change at equilibrium of H_2Q^* into Q^* when equimolecular amounts of H_2Q^* and Q′ are used. Thus, if the system chlorohydroquinone–chloroquinone is a stronger oxidizing agent than the system hydroquinone–benzoquinone, referred to the standard system, chloroquinone will have a higher conversion, (β_0), than benzoquinone. The calculation of the benzoquinone equivalent may be illustrated as follows. The conversion value for 2,6-dichloroquinone is 51.2; that is, one mole of 2,6-dichloroquinone added to one mole of H_2Q^* would cause 51.2% of the latter to be oxidized to Q^*. It is possible to calculate how many moles of benzoquinone it is necessary to add to one mole of H_2Q^* to cause 51.2% of the latter to be oxidized to Q^*, knowing the equilibrium constant for benzoquinone to be 0.114.

$$\frac{(\beta_0)^2}{(1-\beta_0)(X_0-\beta_0)} = 0.114$$

X_0 will be the number of moles of benzoquinone which would be required to cause a conversion equal to β_0, obtained by using only one mole of the quinone in question. X_0 may be called the *benzoquinone equivalent.* Thus 5.2 moles of benzoquinone are necessary to give the same β as is given by one mole of 2,6-dichloroquinone.

Results

Table III gives a list of quinones, with their equilibrium constants, conversions, (β_0), and benzoquinone equivalents, (X_0), in relation to the standard system. For the purposes of comparison, the potentials in the solid, dissolved and gaseous states for the same quinones are given. The latter were determined by Conant and Fieser[2h,k] unless otherwise noted.

TABLE III

CONVERSIONS OF QUINONE–HYDROQUINONE SYSTEMS

Quinone	K (av.)	β_0	X_0	Normal reduction potentials E_0					
				E_s	0.1 N HCl H_2O	1.0 N HCl H_2O	0.5 N HCl alc.-H_2O	1.0 N HCl alc.-H_2O	E_g
p-Xyloquinone	0.00059	2.4	0.03	0.582	0.590	..	0.600	0.597	0.486
Toluquinone	.00437	6.2	0.10	.623	.645	.641	..	.656	..
Benzoquinone	.114	25.2	1.000	.681	.699	.696	..	.711	.570
Chloroquinone	.669	45.0	3.7	.678	.713	.710	..	.736	.611
Bromoquinone	.853	48.0	4.4	..	[7]	..	..	..	..
2,6-Dichloroquinone	1.09	51.2	5.2	.689	.722	.719	..	.748	.636
2,6-Dibromoquinone	1.43	54.5	6.3	..	..	..	..	..	..
Trichloroquinone	..	..	..	.670	..	..	.731	.726	.649
Tetrachloroquinone	1.27	53.0	5.8	.664	..	..	.695	.703	.657
Tetrabromoquinone	1.69	56.5	7.0	..	..	..	..	..	..
2,5-Dichloroquinone	1.73	56.8	7.1	.689	[7]	.719	.740	.734	.
2,5-Dibromoquinone	9.04	75.0	20.5	..	[7]	..	..	..	..

Since conversions and benzoquinone equivalents do not yield to ready comparison with the potentials determined electrochemically, a series of potentials, (E^*), has been calculated from the equilibrium constants given in Table III. This has been accomplished by use of the equation $E = (RT/nF) \log_e K$ in which T is 300. A system which has the same oxidizing strength as the optically active standard system will have a value of E^* equal to zero. Weaker oxidizing systems will have negative values of E^* and stronger oxidizing systems will have positive values of E^*. It is convenient to change the E^* values to a series in which the benzoquinone–hydroquinone system is represented by zero. This series is given in Table IV under the heading ΔE^*.

[7] La Mer and Baker[2f] give the following: chloroquinone, 0.7125; bromoquinone, 0.7151; whereas Biilmann[2i] gives: chloroquinone, 0.7124 and bromoquinone, 0.7120; 2,5-dichloroquinone, 0.7230 and 2,5-dibromoquinone, 0.7228.

In order to calculate the potentials for a system in benzene from the E_g values determined by Conant it would be necessary to know the vapor pressures of the components of the system and their solubilities in benzene. As yet these data are not available. An interesting series of potentials could be calculated if the E_g value of benzoquinone, 0.570, were arbitrarily chosen as the potential of benzoquinone in benzene. To this could be added the ΔE^* values. Since these potentials might be misleading, an alternative procedure has been used. The E_g value of benzoquinone has been set equal to zero and ΔE_g values calculated accordingly. These results are given in Table IV.

TABLE IV

RELATIVE POTENTIALS OF QUINONE–HYDROQUINONE SYSTEMS IN BENZENE

Quinone	$\log_{10} K$	E^*	ΔE^*	ΔE_g
p-Xyloquinone	−3.22915	−0.09613	−0.0681	−0.084
Toluquinone	−2.35952	− .07024	− .0422	.....
Benzoquinone	−0.94310	− .02808	.0000	.000
Chloroquinone	− .17457	− .00520	+ .0229	+ .041
Bromoquinone	− .06905	− .00206	+ .0260	.....
2,6-Dichloroquinone	+ .03743	+ .00111	+ .0292	+ .066
2,6-Dibromoquinone	+ .15534	+ .00462	+ .0327	.....
Tetrachloroquinone	+ .10380	+ .00309	+ .0312	+ .087
Tetrabromoquinone	+ .22789	+ .00678	+ .0349	.....
2,5-Dichloroquinone	+ .23805	+ .00709	+ .0352	.....
2,5-Dibromoquinone	+ .95617	+ .02847	+ .0566	.....

Discussion

The results indicate that this method gives a quantitative evaluation of the oxidizing strength of a series of hydroquinone–quinone systems, compared to a standard system. Certain generalizations are apparent from the data in Table III. A methyl group lowers and a halogen raises the conversion value of the parent compound. Furthermore, a methyl group is more effective than a halogen atom. In general, the successive introduction of like groups causes the conversion values to change consistently in the same direction, the first group always being more effective than the succeeding ones. The position of the groups is of importance since the 2,5-dihalogenated quinones have much higher conversion values than anticipated, even higher than those of the tetrasubstituted quinones. A similar difference due to position was pointed out in the consideration of the rotations of the optically active halogenated hydroquinones, shown in Table I. In both cases this difference is far more marked in the brominated compounds than in the chlorinated compounds. The introduction of bromine gives systems which are stronger oxidizing agents than are the analogous chlorinated systems. The difference between the two is quite uniform except in the abnormal 2,5-dihalogenated quinones.

Comparison with Electrochemical Data.—The relative order of the

potentials of *p*-xyloquinone, toluquinone, benzoquinone and chloroquinone is the same whether the potentials are determined for the solid, dissolved or gaseous state. Thus benzoquinone has a higher potential than has *p*-xyloquinone, in all three states.[2h,k,8] The results obtained in this research also show the same relative order for these four quinones.

However, for the polyhalogenated quinones there is no agreement among the potentials for the three states. The potentials of the tri- and tetrachloroquinones, in the solid state and in solution, are lower than that of benzoquinone. In the gaseous state the potentials of the polychloro compounds are higher than that of benzoquinone. Our results are well in accord with those obtained by Conant for the gaseous state, as can be seen by Table III.

The introduction of two methyl groups into benzoquinone causes a decided drop in both E_g and β_0. The successive introduction of a chlorine atom causes an increase in E_g and β_0, the first chlorine being more effective than the second, and it in turn more effective than the next. Two methyl groups decrease E_g and β_0 to a greater extent than two chloro groups increase them. It would be unwarranted to predict close agreement between the ΔE^* and ΔE_g values, given in Table IV, though values of the same order of magnitude would be expected. Conant did not determine the E_g value of 2,5-dichloroquinone or of any bromoquinones.

Electrochemical studies of analogous chloro and bromo compounds give potentials differing by less than the experimental error. Our method, however, shows that these compounds differ decidedly in oxidizing strength.

The electrochemical results for alcoholic solutions cannot be checked by this method because the optically active quinones do not give reproducible rotations in alcohol. In some cases the rotations are so abnormal as to indicate possible reaction between the quinone and the alcohol. The present method is further limited because a quinone–hydroquinone pair that is weaker in oxidizing strength than is the 2,5-dimethylhydroquinone–quinone pair cannot be measured accurately, due to the low rotations resulting. To overcome this difficulty a new standard pair for a different range must be obtained.

The junior author is continuing the investigation of this field.

Experimental

Experimental Determination of Conversions.—An extensive study of the system hydroquinone–benzoquinone, in the presence of the standard pair, was first carried out. A number of runs at several different concentrations were made to obtain the equilibrium constant. All determi-

[8] Information obtained from absorption spectra of molecular compounds involving these four quinones also indicates the same relative order (unpublished work by W. H. Hunter and E. H. Northey).

nations were made at 27°. A weighed quantity of benzoquinone was added to a weighed sample of H_2Q^*, together with enough benzene to dissolve the two compounds. In a few minutes a green precipitate formed. After letting the solution stand for about two hours, enough benzene was added to dissolve the precipitate, and the whole was diluted to a definite volume. Benzoquinone was the only quinone used that resulted in a precipitation of a quinhydrone. Because of this quinhydrone formation it was possible to arrive at the equilibrium point much sooner than in any other case.

TABLE V

EQUILIBRIUM CONSTANTS OF SYSTEM STANDARD PAIR—BENZOQUINONE–HYDROQUINONE

H_2Q^* (g.)	$\frac{\text{Moles Benzo Q}}{\text{Moles } H_2Q^*}$	β	K	K (av.)
0.1825	1	25.0	0.111	
.1823	1	24.8	.109	
.1311	1	25.2	.114	0.111
.1980	2	35.1	.115	
.1815	2	36.2	.125	
.1859	2	34.2	.107	
.1281	2	35.0	.114	
.1275	2	35.8	.122	
.1826	2	35.4	.118	.117
.1765	3	41.4	.113	
.1862	3	41.9	.117	
.1016	3	40.5	.106	.115
.1040	4	46.1	.112	.112
			Average of K's	.114

$\beta_0 = 25.2$ for benzoquinone.

The equilibrium was now approached from the other side. Hydroquinone was added to an equimolecular amount of Q*. The hydroquinone was dissolved in warm benzene and cooled before it was added to Q*, since hydroquinone dissolves very slowly in benzene. No quinhydrone formed in this experiment. The rotation slowly dropped during the first twenty-four hours and then remained constant for about twenty hours before it began to drop again. From the rotation at equilibrium it was determined that 74.9% of the optically active quinone had been converted into the H_2Q^*. This value agrees very well with the conversion value (β_0) of 25.2%.

Below are given the results of a typical determination, using an equimolecular mixture of 2,6-dichloroquinone and H_2Q^*.

0.1228 g. of H_2Q^* 0.0618 g. of 2,6-dichloroquinone

$\frac{0.1228}{0.1240} \times 0.24 = 0.238° = A$ = rotation due to H_2Q^* in 25 cc. benzene, 2-dec. tube

$\frac{0.1228}{0.1042} \times \frac{350}{352} \times 1.82 = 2.180° = B$ = rotation if all of H_2Q^* were changed to Q*, in 25 cc. benzene, 2-dec. tube.

The two compounds were dissolved in 25 cc. of benzene and allowed to stand for thirteen hours before being diluted to 50 cc.

TABLE VI

DETERMINATION OF THE CONVERSION OF 2,6-DICHLOROQUINONE

l, dm.	Benzene, cc.	Zero	Obs.	$\alpha = c$	β	A	B	$B - A$	$C - A$	Time, hrs.
3	50	5.13	5.85	0.72	37.2	0.178	1.635	1.457	0.542	14
3	75	5.13	5.70	.57	46.5	.119	1.090	0.971	.451	20
3	75	5.13	5.72	.59	48.5	.119	1.090	.971	.471	24
3	75	5.13	5.74	.61	50.6	.119	1.090	.971	.491	36
3	100	5.13	5.59	.46	51.0	.089	0.817	.728	.371	39
3	100	5.13	5.59	.46	51.0	.089	.817	.728	.371	48
3	100	5.13	5.52	.39	41.3	.089	.817	.728	.301	60

$$\beta = \frac{C - A}{B - A}$$

$\beta_0 = 51.0$ for this determination.

TABLE VII

EQUILIBRIUM CONSTANTS OF STANDARD PAIR—QUINONE–HYDROQUINONE PAIRS

Quinone	H_2Q*, moles	Q, moles	β	K	K (av.)
Monochloroquinone	1	1	45.0	0.669	
	1	1	45.0	0.669	0.669
2,5-Dichloroquinone	1	0.75	48.4	1.71	
	1	0.75	48.0	1.64	
	1	1.00	56.5	1.69	
	1	1.00	57.4	1.82	
	1	1.00	57.0	1.76	1.73
2,6-Dichloroquinone	1	0.75	44.0	1.11	
	1	1.00	51.0	1.08	1.09
Tetrachloroquinone	1	0.50	35.1	1.27	
	1	1.00	53.0	1.27	1.27
Monobromoquinone	1	0.75	40.9	0.830	
	1	0.75	40.7	0.815	
	1	0.80	43.0	0.877	
	1	1.00	48.4	0.880	
	1	1.00	47.2	0.799	
	1	1.50	58.7	0.914	0.853
2,5-Dibromoquinone	1	0.50	45.7	8.95	
	1	0.80	65.8	8.92	
	1	0.80	66.0	9.15	
	1	1.00	75.0	9.00	
	1	1.00	75.2	9.20	9.04
2,6-Dibromoquinone	1	0.50	35.9	1.43	
	1	0.75	46.5	1.42	
	1	0.75	46.3	1.39	
	1	1.00	53.0	1.49	1.43
Tetrabromoquinone	1	0.50	36.9	1.65	
	1	0.50	37.4	1.77	
	1	1.00	56.8	1.73	
	1	1.00	55.9	1.61	1.69

TABLE VII (*Concluded*)

Quinone	H_2Q,* moles	Q, moles	β	K	K (av.)
Toluquinone	1	1.00	6.3	0.00452	
	1	2.00	8.6	.00423	
	1	3.00	10.6	.00434	0.00437
p-Xyloquinone[9]	1	1.00	2.3	.00056	
	1	3.00	4.2	.00062	0.00059

Preparation of Materials

The common derivatives of benzoquinone were prepared by the ordinary methods. Zinc *d*-camphorsulfinate was made according to the method of Smiles and Hilditch.[10]

***d*-Camphorsulfones of Hydroquinones.**—The quinone, dissolved in alcohol, was added slowly to an excess of zinc *d*-camphorsulfinate, dissolved in dilute acid. The reaction was very rapid in the case of benzoquinone and the halogenated quinones and the yellow color of the quinone disappeared very rapidly. On standing for a few hours or by concentration *in vacuo* precipitation took place or an oil settled out. In the latter case several days was sometimes necessary to effect crystallization. The sulfones are quite soluble in all the common organic solvents. Recrystallization is accomplished from dilute alcohol. The *d*-camphorsulfone of 2,5-dimethylhydroquinone when dissolved in alcohol is easily precipitated, by the addition of water, to give a cotton-like mass. The hydroquinones are soluble in alkali and are reprecipitated by the addition of acids, but are not obtained in a pure state. The hydroquinones give no color with ferric chloride but reduce an ammoniacal silver nitrate solution. By dissolving a small amount of any one of these hydroquinones, together with a little benzoquinone, in ether a small amount of a purple quinhydrone remains on evaporation of the solvent. The hydroquinones are white and odorless. The yields are practically quantitative.

Hydroquinone *d*-Camphorsulfone. Melting point 159–160°, $[\alpha]^{27}_{5461}$ +46.55, c = 0.3366 in benzene, α = 0.47°, l = 3.

Anal. Calcd. for $C_{16}H_{20}O_5S$: C, 59.26; H, 6.17. Found: C, 59.25; H, 6.7.

Diacetate of Hydroquinone *d*-Camphorsulfone.—This was obtained by treating the hydroquinone with acetic anhydride. It was recrystallized from aqueous alcohol. It is soluble in organic solvents and insoluble in water or alkali; m. p. 119–122°. The rotation of the diacetate is slightly lower than that of the hydroquinone, $[\alpha]^{27}_{5461}$ +17.5, c = 0.5448 in abs. alc., α = 0.18°, l = 2.

Anal. Calcd. for $C_{20}H_{24}O_7S$: C, 58.8; H, 5.9. Found: C, 58.7; H, 5.9.

2,5-Dichlorohydroquinone *d*-Camphorsulfone.—M. p. 169–173°, $[\alpha]^{27}_{5461}$ +29.99, c = 0.3398 in benzene, α = 0.305°, l = 3.

Anal. Calcd. for $C_{16}H_{18}O_5Cl_2S$: C, 48.86; H, 4.6. Found: C, 49.0; H, 4.6.

2,6-Dichlorohydroquinone *d*-Camphorsulfone.—M. p. 104–106°, $[\alpha]^{27}_{5461}$ +35.4°, c = 0.3716 in benzene, α = 0.395°, l = 3.

Anal. Calcd. for $C_{16}H_{18}O_5Cl_2S$: C, 48.86; H, 4.6. Found: C, 48.91; H, 4.6.

2,5-Dibromohydroquinone *d*-Camphorsulfone.—M. p. 172–173°, $[\alpha]^{27}_{5461}$ +19.6°, c = 0.5260 in benzene, α = 0.31°, l = 3.

Anal. Calcd. for $C_{16}H_{18}O_5Br_2S$: C, 39.83; H, 3.74. Found: C, 39.55; H, 4.0.

[9] The results for *p*-xyloquinone are not as reliable as for the other quinones since the observed rotations were close to that due to the unchanged optically active hydroquinone added.

[10] Smiles and Hilditch, *J. Chem. Soc.*, **91**, 519 (1907).

2,6-Dibromohydroquinone *d*-Camphorsulfone.—M. p. 108–112°, $[\alpha]^{27}_{5461}$ +37.9°, c = 0.3568 in benzene, α = 0.395°, l = 3.

Anal. Calcd. for $C_{16}H_{18}O_5Br_2S$: C, 39.83; H, 3.74. Found: C, 40.7; H, 4.4.

2,5-Dimethylhydroquinone *d*-Camphorsulfone.—M. p. 176–177°, $[\alpha]^{27}_{5461}$ +24.22, c = 0.4960 in benzene, α = 0.24°, l = 2.

Anal. Calcd. for $C_{18}H_{24}O_5S$: C, 61.36; H, 6.82. Found: C, 61.12; H, 6.84.

Diacetate of 2,5-Dimethylhydroquinone *d*-Camphorsulfone.—M. p. 103–106°, $[\alpha]^{27}_{5461}$ +21.7°, c = 0.4758 in benzene, α = 0.31°, l = 3.

Anal. Calcd. for $C_{22}H_{28}O_7S$: C, 60.55; H, 6.42. Found: C, 60.50; H, 6.47.

The *d*-Camphorsulfones of Quinones.—The *d*-camphorsulfones of benzoquinone and *p*-xyloquinone were prepared by oxidation of the corresponding hydroquinones. The latter were dissolved in ether and an excess of either lead dioxide or silver oxide was added. The mixture was stirred from three to ten minutes and was then filtered. The residue was well washed with dry ether. The combined ether filtrates were concentrated, using a water pump. The yellow quinones crystallized from the concentrated solutions. The quinones were filtered off and washed with a little cold ether. The yields ranged from 30 to 80%.

The optically active quinones are yellow, crystalline compounds, quite soluble in alcohol, benzene, chloroform, acetic acid and acetone. They are less soluble in ether and are insoluble in water. They are not volatile with steam and do not have an odor. The values for their specific rotations are considerably higher than those of the corresponding hydroquinones. In the case of the *d*-camphorsulfone of benzoquinone the rotation in alcohol is very little higher than that of the hydroquinone, but in benzene solution there is a considerable difference in their rotations.

Benzoquinone *d*-Camphorsulfone.—M. p. 135–136°, $[\alpha]^{27}_{5461}$ +305°, c = 0.5696 in benzene, α = 3.48°, l = 2.

Anal. Calcd. for $C_{16}H_{18}O_5S$: C, 59.63; H, 5.6. Found: C, 59.73; H, 5.7.

***p*-Xyloquinone *d*-Camphorsulfone.**—M. p. 148–151°, $[\alpha]^{27}_{5461}$ +223°, c = 0.4168 in benzene, α = 1.86°, l = 2.

Anal. Calcd. for $C_{18}H_{22}O_5S$: C, 61.7; H, 6.3. Found: C, 61.7; H, 6.7.

α-Naphthoquinone *d*-Camphorsulfone.—α-Naphthoquinone was added to *d*-camphorsulfinic acid. The expected hydroquinone was impure due to partial oxidation to the quinone. This impure product was oxidized in the usual manner to give the optically active quinone, m. p. 144–148°, $[\alpha]^{27}_{5461}$ +237.3°, c = 0.3224 in benzene, α = 1.53°, l = 2.

Anal. Calcd. for $C_{20}H_{20}O_5S$: C, 64.5; H, 5.4. Found: C, 64.0; H, 5.6.

Attempted Preparation of Hydroquinone *d*-Bromocamphorsulfone.—It was supposed that the *d*-bromocamphorsulfone of hydroquinone would have a higher rotation than has the unbrominated compound. However, it was found that the zinc–absolute alcohol reduction of *d*-bromocamphorsulfonyl chloride gave zinc *d*-camphorsulfinate instead of the desired zinc *d*-bromocamphorsulfinate.

Summary

1. A number of optically active quinones and hydroquinones have been prepared.

2. The effect of substitution on their rotations has been determined.

3. The oxidizing strength of a number of hydroquinone–quinone pairs has been measured by use of a standard optically active hydroquinone–quinone pair.

4. The effect of substitution on the oxidizing power of a hydroquinone–quinone system has been shown.

5. The results thus obtained have been compared with the electrochemical data in the form of oxidation–reduction potentials.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A QUANTITATIVE STUDY OF SEMICARBAZONE FORMATION

BY JAMES B. CONANT AND PAUL D. BARTLETT

RECEIVED FEBRUARY 10, 1932 PUBLISHED JULY 6, 1932

The interaction between ketones or aldehydes and such substances as phenylhydrazine and hydroxylamine has been the subject of numerous investigations in which the rate of the reaction has been measured. Most of these studies, however, were carried out before the use of the hydrogen electrode had enabled the chemist to define with precision the acidity of his solutions.[1] In recent years it has become apparent that in all these reactions one is dealing with a reversible reaction in which the acidity of the medium plays an important role in determining both the rate of the reaction and the final equilibrium which is reached. The early work of Acree and of Lapworth considered the influence of these factors to the extent that was possible at that time. The recent work of Ölander on the formation of acetoxime is the most complete study of this type of reaction from the modern viewpoint. This work will be referred to again in connection with our own measurements.

We have undertaken to study semicarbazone formation by a variety of carbonyl compounds in aqueous buffer solutions. Our results show the conditions which control the equilibrium in this reaction and the factors which influence the rate of the process. It seems probable that the fundamental principles which we believe we have elucidated can be applied to other similar reactions such as phenylhydrazone and oxime formation; these reactions, therefore, will be briefly discussed in the appropriate place in this paper. We shall first present our own results which are concerned with the equilibrium, then the kinetic study and finally a discussion of the influence of the structure of the carbonyl compound on both the composition of the equilibrium mixture and the rate at which this equilibrium is reached.

[1] The following references are among the most important: (a) Acree and Johnson, *Am. Chem. J.*, **38**, 308 (1907); Acree, *ibid.*, **39**, 300 (1908); (b) Barrett and Lapworth, *J. Chem. Soc.*, **93**, 85 (1908); (c) Ölander, *Z. physik. Chem.*, **129**, 1 (1927); (d) Bodforss, *ibid.*, **109**, 223 (1924); (e) Petrenko-Kritschenko and co-workers, *Ann.*, **341**, 150 (1905); *Ber.*, **34**, 1702 (1901); **39**, 1452 (1906); (f) Stewart, *J. Chem. Soc.*, **87**, 410 (1905); (g) Grassi, *Gazz. chim. ital.*, **38**, II, 32 (1908); *ibid.*, **40**, II, 139 (1910); (h) Michael, THIS JOURNAL, **41**, 393 (1919); (i) Ardagh and Williams, THIS JOURNAL, **47**, 2976, 2983 (1925).

I. Equilibrium Measurements

The reaction between a carbonyl compound AO and a carbonyl reagent such as semicarbazide, phenylhydrazine or hydroxylamine BNH_2 is a reversible reaction; it is convenient to regard this reaction as an hydrolysis of the condensation product and write the reaction:

$$A{=}NB + H_2O \rightleftharpoons AO + BNH_2$$

The reagent, BNH_2, is a base whose conjugate acid is BNH_3^+ and the condensation product is similarly related to the acid $A{=}NBH^+$. We may write for the two acid–base equilibria the following equations in which the concentrations are denoted by the square brackets; these are the limiting laws holding in very dilute solution, and the relationships we shall derive with their use are subject to this same limitation. The probable error introduced by assuming their validity in solutions containing considerable salt will be discussed later.

$$K_R = \frac{[BNH_2]\,[H^+]}{[BNH_3^+]} \tag{1}$$

$$K_C = \frac{[ANB]\,[H^+]}{[ANBH^+]} \tag{2}$$

For the reversible formation of the condensation product A = NB we may define a constant which corresponds to the equilibrium in a solution so strongly acid that no appreciable quantity of the reagent or condensation product is uncombined with a proton. This is the limiting hydrolysis in acid solutions

$$K_{\infty A} = \frac{[AO]\,[BNH_3^+]}{[ANBH^+]} \tag{3}$$

If there are no appreciable quantities of intermediate compounds (such as the hypothetical direct addition product of the reagent and carbonyl compound) we may write for the hydrolysis of the condensation product in a solution of any acidity the equation (where K is a constant only at constant acidity).

$$K = \frac{[AO]\,([BNH_3^+] + [BNH_2])}{[ANB] + [ANBH^+]} \tag{4}$$

Substituting values of $[BNH_2]$ and [ANB] from equations 1 and 2 into 4, we find the following relation between K, $K_{\infty A}$, K_R and K_C (equation 5)

$$K = K_{\infty A}\,\frac{[H^+] + K_R}{[H^+] + K_C} \tag{5}$$

When $[H^+]$ is small compared to K_R and K_C, we have the limiting value of K for the case where the solution is so weakly acid that no appreciable quantity of the reagent or condensation product is combined with a proton. This limiting value will be denoted as $K_{\infty B}$

$$K_{\infty B} = K_{\infty A}\,\frac{K_R}{K_C} \tag{6}$$

It is clear that the ratio of the equilibrium constants in very acid and basic solutions is a function of the difference in acid strength of the ions BNH_3^+

and $ANBH^+$. Expressed logarithmically $pK_{\infty B} - pK_{\infty A} = pK_R - pK_C$. It is interesting to note that when the hydrolysis constant (K) is midway between its limiting values, $[H^+] = K_C$ or $pH = pK_C$; that the inflection of the pH:K curve must occur at this point can be shown by differentiation of equation 5.

The data we have obtained on the equilibrium involving the hydrolysis of acetone semicarbazone illustrates the application of the equations we have just developed. The data are summarized in Table I and shown graphically in Fig. 1. The experimental procedure consisted in dissolving the semicarbazone in an aqueous buffer solution containing in some cases a definite quantity of acetone to suppress the hydrolysis, and removing samples from time to time and titrating with iodine at a P_H of about 7 obtained by using a concentrated phosphate buffer solution. This method of determining semi-

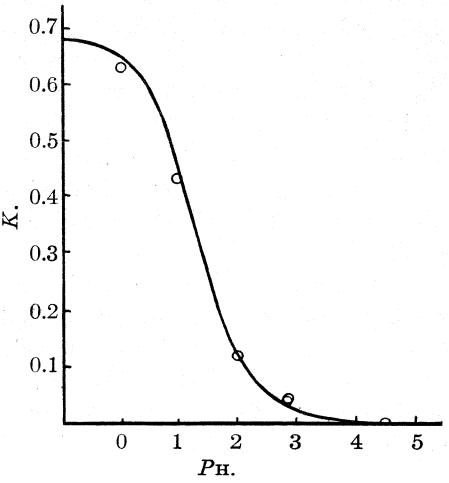


Fig. 1.—Variation of hydrolysis constant of acetone semicarbazone with P_H at 25°.

TABLE I

HYDROLYSIS OF ACETONE SEMICARBAZONE AT 25.00 ± 0.01°

For the composition of the buffer solutions employed, see Table VIII.

P_H of buffer	Initial concn. of acetone semicarbazone, moles × 10^{-3} per liter	Initial concn. of acetone, moles per liter	0.2304 N iodine for 10.14-cc. sample, cc.	Concn. of semicarbazide at equilibrium, moles × 10^{-3} per liter	K	K_C (by equation 7)
0	2.45	0.270	3.33			
			3.33	1.72	0.633	0.0443
1.00	2.73	.257	3.34			
			3.33	1.72	.435	.0416
			3.26			
2.02	2.63	.303	1.48			
			1.53	0.076	.122	.0532
2.84	3.76	.0752	2.10			
			2.26	1.29	.0379	(− .0451)
			2.27			
2.87	2.73	.257	0.81			
			.72	0.39	.0426	(− .0314)
			.76			
4.50	2.63	0	3.34	1.72	.00324	.....
			3.33			

carbazide has recently been published.[2] The chief sources of error in the determination of the hydrolysis constant are the slowness with which final equilibrium is reached and the appreciable decomposition of semicarbazide into hydrazine and hydrazodicarbamide. This decomposition slowly displaces the equilibrium in such a way as to increase the iodine equivalent of the solution. The two sources of error thus work in opposite directions, and where the rate of hydrolysis was such that equilibrium was reached in a few hours, the results are more reliable than in those cases where several days were required. Several samples were always taken from the reaction mixture and titrated at successive times sufficiently far apart to ensure equilibrium being reached.

In the case of acetone semicarbazone the limiting hydrolysis on the weakly acid side is sufficient so that the value of $K_{\infty B}$ can be measured experimentally and is clearly the value of K obtained at P_H values of 4, 5 and 7 (0.0032–0.0034). With this value and the dissociation constant of semicarbazide $K_R = 0.000219$, one can obtain the value of K_C from each value of K by combining equations 5 and 6 to yield 7. The values thus

$$K_C = \frac{[H^+]}{\frac{K_{\infty B}}{KK_R}([H^+] + K_R) - 1} \qquad (7)$$

obtained (last column of Table I) were satisfactory except with the two citrate buffer solutions, in which case impossible negative values were obtained. The curve in Fig. 1 is drawn with the constants $K_R = 0.000219$, $K_{\infty B} = 0.0032$ and $K_C = 0.0463$ which yield $K_{\infty A} = 0.69$. The agreement is all that can be expected considering the experimental difficulties and the uncertainties involved in applying equations developed for very dilute solutions to those containing considerable salt.[3] It will be noted that the acid limit of hydrolysis is very nearly reached in 1.2 M hydrochloric acid, so that with acetone semicarbazone the whole curve can be realized experimentally.

In the case of the semicarbazones of aromatic aldehydes the hydrolysis is so slight in the more basic solutions that no direct measure of $K_{\infty B}$ is possible. Portions of the $P_H : K$ curve lying in the more acid regions can be estimated from values of K obtained at different P_H values. Since two unknown constants, K_C and $K_{\infty A}$ (or $K_{\infty B}$ if one desires), are involved, the best curve through the experimental points can be obtained by a trial and error graphical method. It was found more convenient, however,

[2] Paul D. Bartlett, THIS JOURNAL, **54**, 2853 (1932).

[3] The buffer solutions employed (see Table VIII) varied in ionic strength from 0.045 to 1.28; the value of K_R taken corresponds to an ionic strength of 0.08. The errors introduced by the effect of changing ionic strength and individual ion effects on the values of K_R, K, K_C and $K_{\infty B}$ have been neglected. It is doubtful in the present case whether the equilibrium measurements are of sufficient precision to warrant a consideration of these factors.

to determine the most probable values of the two constants by an application of the method of least squares.

The observational equations were in the form $aK_{\infty A} + bK_C = q$ and by the theory of normal equations the most probable values of the two constants were obtained by solving the equations

$$\Sigma(aa)\ K_A + \Sigma(ab)\ K_C = \Sigma(aq) \text{ and } \Sigma(ab)\ K_\infty A + \Sigma(bb)\ K_C = \Sigma(bq)$$

The values thus calculated are given in Table II for the semicarbazones of furfural, acetaldehyde and benzaldehyde. In the case of the first compound, equilibrium was approached from the side of the aldehyde and semicarbazide; with the other two the same procedure was used as with acetone semicarbazone. In Table II are recorded the observed values of K (the hydrolysis constant) at the different P_H values and the value of K calculated with the aid of K_C and $K_{\infty A}$ determined as just described. A comparison of the observed and calculated values of K shows that equation 4 is a satisfactory formulation of the hydrolysis equilibrium in these cases. It is evident that the limit of acid hydrolysis ($K_{\infty A}$) should be nearly reached at a P_H value of 0. With furfural semicarbazone, however, absurd values of K, some 200 times too large, were obtained with a 1.2 M solution of hydrochloric acid. It seems that some side reactions were involved in this strong acid solution.

TABLE II

HYDROLYSIS OF SEMICARBAZONES AT DIFFERENT P_H VALUES AT 25.00 ± 0.01°

	Semicarbazones of							
	Furfural		Acetaldehyde		Benzaldehyde		Pyruvic acid	
P_H	$K \times 10^4$ obs.	$K \times 10^4$ calcd.	$K \times 10^4$ obs.	$K \times 10^4$ calcd.	$K \times 10^4$ obs.	$K \times 10^4$ calcd.	$K \times 10^4$ obs.	$K \times 10^4$ calcd.
−0.01	72000							
1.00	9.37	9.12	45	44	7.6	7.6	2.95	3.06
2.02	2.10	2.65	9.3	8.5	1.34	1.24	0.69	0.55
2.44	1.13	1.20						
2.88	0.56	0.51			0.23	0.21	.18	.19
2.93	.40	.43						
3.24	.32	.27						
3.40	.20	.21						
3.95	.15	.11	0.27	0.32				
4.00							.089	.069
7.00			.29	.21			.051	.051

Constants used for calculating K are given in Table IIa.

TABLE IIa

SUMMARY OF HYDROLYSIS CONSTANTS OF DIFFERENT SEMICARBAZONES AT 25.00 ± 0.01°

Semicarbazone of	K_C	Acid limit $K_{\infty A}$	Basic limit $K_{\infty B} \times 10^3$	pK_C	$pK_{\infty A}$	$pK_{\infty B}$
Furfural	0.036	0.0012	0.0076	1.44	2.92	5.42
Acetaldehyde	.078	.0076	.021	1.10	2.12	4.68
Benzaldehyde	.111	.0015	.0030	0.96	2.82	5.52
Pyruvic acid	.258	.0010	.0051	.59	3.00	5.29
Acetone	.046	.69	3.24	1.33	0.16	2.49

Pyruvic Acid Semicarbazone.—In the case of pyruvic acid we have an interesting example of a carbonyl compound which also enters into an acid-base equilibrium, so that the behavior of its semicarbazone would be expected to differ from that of a semicarbazone of an ordinary ketone or aldehyde. The limiting basic hydrolysis equilibrium is one between neutral semicarbazide, the negative ion of pyruvic acid and the negative ion of the semicarbazone.

The results are included in Table II, the value of K_A for pyruvic acid being taken as 0.0056.[4] It seems most reasonable to attribute the value of K_C to the compound $HPNBH^+$, regarding the uncharged form of pyruvic acid semicarbazone as the molecular form $CH_3C(COOH)=NNHCONH_2$, and not an "inner-salt" form. The hydrolysis of pyruvic acid semicarbazone increases with acidity more slowly than the hydrolysis of the other semicarbazones. This is due to the tendency of the semicarbazone $CH_3C(COO^-)=NNHCONH_2$ to take on a hydrogen ion at the carboxyl group, which occurs in approximately the same P_H range as the taking of a hydrogen ion by the free semicarbazide. In their effects upon hydrolysis constant these two changes work against each other. Therefore pyruvic acid is well adapted for regenerating ketones and aldehydes from their semicarbazones and similar derivatives, working either in acid solutions (as with 10% neutralized pyruvic acid) or with the sodium salt of pyruvic acid in neutral solution. The low limiting value of the hydrolysis constant which is more like that of an aldehyde semicarbazone than a ketone semicarbazone is, of course, of fundamental importance in this connection. Such a use of pyruvic acid has been suggested by Grassi, and by Sidgwick.[1g,5]

We may now consider briefly the equilibria which are concerned with the hydrolysis (or formation) of oximes and phenylhydrazones. If we may make the same assumption as in the case of semicarbazone formation that there are no appreciable quantities of intermediates in the equilibrium mixture, the equations developed above should apply directly to the hydrolysis of these other condensation products. The only adequate data available to test this point seem to be those of Ölander on the equilibria in acetoxime formation in buffer solutions from P_H 1.22 to 5.27. We have calculated from Ölander's values of $1/K$ (since he expressed his equilibrium constant in the inverse form from our equation), the most probable values of K_C and $K_{\infty A}$ taking his value of K_R for hydroxylamine as 8.05×10^{-7}. The following table (Table III) shows that except at the extreme end of his range, the agreement between $1/K$ calculated, and observed, is excellent, showing the applicability of equation 5 to the hydrolysis of oximes.

The acid dissociation constant of the acetoxime ion $(CH_3)_2C=NH^+OH$ by this computation is 0.012 or $pK_C = 1.92$; from the values in the litera-

[4] Hantzsch and Miolati, *Z. physik. Chem.*, **10**, 1 (1892).

[5] Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1910, p. 247.

TABLE III

HYDROLYSIS OF ACETOXIME AT 20.0° (DATA OF ÖLANDER)

P_H	Equilibrium constant $1/K$ obs.	$1/K$ calcd.	Deviation, %	P_H	Equilibrium constant $1/K$ obs.	$1/K$ calcd.	Deviation, %
1.22	54.1	85	+57	3.15	1428	1286	−10
1.70	103.0	114	+11	3.41	2500	2273	− 9.1
1.74	106.8	118	+10.5	3.50	3060	2780	− 9.1
2.15	203.4	192.6	− 5.3	3.80	5120	5453	+ 6.5
2.18	215.2	201.3	− 6.5	4.25	16250	15207	− 6.4
2.58	475.5	396.9	−16.5	4.86	55700	57729	+ 3.6
2.65	560	455.1	−18.9	5.27	71000	139088	+96

The calculated values of K were obtained using equation 5 and the values: $K_{\infty A} = 14 \times 10^{-3}$; $K_R = 8.05 \times 10^{-7}$; $K_C = 12 \times 10^{-3}$.

ture it appears[6] that K_B (the old basic dissociation constant) is about 6×10^{-13}; this corresponds to pK for the acid ion of 1.78 in good agreement with our value. It is clear from an inspection of the values given in Table IIa for the dissociation constant of the acid ion of the semicarbazone (pK_C) that they differ not more than half a pK unit from a mean value of 1.1. It is not certain that this variation really represents differences in the acid–base equilibria of the condensation product as some of the errors of the equilibrium measurements are reflected in these constants. The acetoxime ion appears to be a weaker acid than the corresponding semicarbazone ion by about one pK unit (*i. e.*, acetoxime is a somewhat stronger base); however, the closeness in the two acid constants shows that the acid dissociation of the ion $R_2C{=}NH^+B$ is not very dependent on the nature of B.

It is interesting to compare the common carbonyl reagents in regard to the hydrolysis of their condensation products with acetone, and the effect of changing hydrogen-ion concentration on the equilibrium. In Table IV are collected values for $pK_{\infty B}$ for acetoxime (Ölander's data), acetone phenylhydrazone (some preliminary unpublished data) and acetone semicarbazone, the values of pK for the acid dissociation constant of the reagent BNH_3^+ (pK_R) and for the condensation product (pK_C); the value of $pK_{\infty A}$ was calculated by equation 6. If one assumes that pK_C for a phenylhydrazone is the same as for a semicarbazone, $pK_{\infty A}$ for phenylhydrazine would be −1.1.

TABLE IV

A COMPARISON OF THE CONSTANTS INVOLVED IN THE EQUILIBRIUM BETWEEN ACETONE AND THREE COMMON CARBONYL REAGENTS

Reagent	pK_R	pK_C	$pK_R - pK_C$	$pK_{\infty B}$ (at 25°)	$pK_{\infty A}$
Hydroxylamine	6.09 (at 20°)	1.92	4.2	6.03	1.8
Phenylhydrazine	5.21 (at 15°)	...	...	2.76	...
Semicarbazide	3.66 (at 25°)	1.33	2.3	2.49	0.16

[6] Scudder, "Electrical Conductivity and Ionization Constants of Organic Compounds," New York, 1914.

It is clear from the values of $pK_{\infty B}$ and $pK_{\infty A}$ that the oximes are much less hydrolyzed than the phenylhydrazones or the semicarbazones and that the difference between the classes of compounds is more pronounced in weakly acid solutions than in strongly acid solutions.

The hydrolysis constant of acetone semicarbazone was determined at P_H 7 at 0°—the value of $K_{\infty B}$ thus obtained was 0.00073 as compared with 0.00324 at 25°. A substitution of these values in the usual integrated form of the Van't Hoff equation yields $\Delta H_{298} = +9700$ cal. for the hydrolysis of acetone semicarbazone to acetone and free semicarbazide in very dilute aqueous solution. ΔF_{298} for the same process is $-1365 \log 0.00324 = +3400$ cal., from which $T\Delta S$ equals 6300 cal. or $\Delta S = 21.1$ E. U.

II. Kinetic Measurements

It has been known for some time that the rate of reaction of ketones and aldehydes with reagents of the type BNH_2 is a function of the acidity of the medium. Acree and Johnson showed that oxime formation was catalyzed by acids and Barrett and Lapworth, working on the formation of acetone and acetaldehyde oximes, found an optimum concentration of acid, above and below which the velocity decreased sharply. Ölander investigated this phenomenon with more care and put forward a hypothesis, accounting for it as purely an effect of hydrogen ion activity. The work of Brönsted has shown that in many reactions it is not solely the hydrogen ion (H_2OH^+) which is the catalyst but that other acids present in the solution[7] may be effective in increasing the rate of the reaction. In general with those reactions which are subject to acid catalysis, the rate is proportional to the concentration of each species of acid present and a constant characteristic for the acid in question. These catalytic constants roughly parallel the acid dissociation constants of the acid, and for this reason if one is using a series of buffer solutions of about the same concentrations true acid catalysis may be overlooked and erroneously believed to be merely hydrogen ion catalysis. To determine whether or not the rates were solely a function of the P_H of the buffer solution or whether catalytic effects were at work, we measured the rate of formation of furfural semicarbazone in an acetate buffer of constant P_H but varying concentration of acetic acid and acetate ions.

Measurement of Velocity Constants.—It has been customary, apparently, in studies of this type of bimolecular reaction, to introduce the two reactants in exactly equal concentrations. This simplifies the mathematical treatment if the reaction is irreversible, but for reversible reactions it makes the treatment unnecessarily difficult. The logarithmic integration of the differential equation for such a process is not suitable for exact

[7] Brönsted, *Chem. Rev.*, 5, 231–338 (1928); Brönsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927).

computation in those cases where the reaction is almost irreversible. However, by maintaining a difference in concentration of the two reactants, it is possible to determine the velocity constants in both directions in a reversible reaction, from a single run and by a single equation with which it is easy to compute. There are three constants which must be known: the difference in concentration of the two reactants (called c in these formulations), the equilibrium constant K and either the initial concentration of a reactant or its concentration at equilibrium (one of these can be derived from the other). These are expressed by x_0 and x_e, respectively.

For a reversible bimolecular reaction in which a single molecule of product is formed by combination of one molecule of each reactant, where the concentrations of the reactants are x and $(x + c)$, respectively, and the equilibrium constant for the reverse reaction $K = k_1/k_2 =$ the ratio of the backward to the forward rate

$$-\mathrm{d}x/\mathrm{d}t = k_2x(x + c) - k_1(x_0 - x)$$

where x_0 is the initial concentration of x; or

$$k_2\mathrm{d}t = \frac{-\mathrm{d}x}{x(x + c) - K(x_0 - x)}$$

The integrated equation takes on the final form

$$k_2t = \frac{2.303}{(2x_e + c + K)} \log \frac{x + (x_e + c + K)}{x - x_e} + C$$

Since the quantities in parentheses are all made up of constants known or measured in the course of the reaction, this equation reduces for a special run to a very simple form in which, especially with a calculating machine, the values of x can be rapidly and easily substituted. It is equally easy to determine k_1 directly from the original equation, or to find it as the product Kk_2.

The integration constant is evaluated if desired by taking x_0 as one of the values of x. In certain cases in this work, x_0 is known with certainty (for example, in all runs at room temperature when the P_H is 7 or less) and in these cases the integration constant is incorporated in the logarithmic formula. At 0°, where the coefficients of expansion were not allowed for in calculating the molarity, and in the alkaline buffers, where addition of semicarbazide was followed by some immediate decomposition by dissolved air, the first determined value of x was sometimes more reliable than the calculated x_0. In these cases the integration constant was not determined, but was canceled out in taking the differences of the logarithms.

It will be seen that this equation reduces to the equation for an irreversible reaction in the special case where x_e and K are equal to zero, for it becomes

$$k_2t = \frac{2.302}{c} \log \frac{x + c}{x} + C$$

This form was used for reactions in which x_e and K were too small to affect the value of the logarithm.

The concentration of reactants was usually chosen which would give not more than 80% reaction in five minutes. The usual velocity run included five titrations, covering about 80% reaction. Whenever there was a measurable equilibrium, the reversible-reaction formula was used in calculating the constants.

The most careful measurements were those in which the sampling was done at one-minute intervals. The 250-cc. glass-stoppered flask containing 200 cc. of buffer solution and 5 cc. of standard furfural solution (previously added from a pipet) and the bottle of standard semicarbazide hydrochloride were brought to temperature in the thermostat. Just before starting the run, the flask was removed and dried, and its stopper, on the inside of which a small inverted weighing bottle was sealed with de Khotinsky cement, was removed and inverted; 5 cc. of the semicarbazide hydrochloride solution was pipetted into the little bottle and at the moment of starting the run the stopper was inserted into the flask and the whole vigorously shaken, resulting in practically instantaneous mixing, as the timing was begun. The flask was replaced in the thermostat, and samples were taken at the stated intervals and added to successive flasks containing a measured amount of iodine, and enough disodium phosphate to bring the P_H of the mixture to 7. Immediately after addition of a reaction sample, the excess of iodine was destroyed by thiosulfate from a pipet. After the five minutes, the excess thiosulfate in each flask was titrated with iodine.

TABLE V

RATE OF FORMATION OF FURFURAL SEMICARBAZONE IN ACETATE BUFFERS OF VARYING CONCENTRATION BUT CONSTANT IONIC STRENGTH

P_H, 4.4; Temp., 25.0 ± 0.01°; μ, 0.694

Total concn. of acetate ion plus acetic acid, moles per liter	0.0302	0.0477	0.0691	0.1257	0.742[a]	0.742[a]
Constant of rate of semicarbazone formation k_2	22.5	31.5	40.4	55.6	102.9	108.4

[a] The ionic strength here was 0.74.

The ionic strength of the solutions dilute in acetate was made up by the addition of potassium chloride. The ratio of acetate ion to acetic acid throughout was 1.7. Two experiments at a molarity of 0.069 with an ionic strength of 0.069 gave values of k_2 of 36.6 and 37.9, showing that a large change of ionic strength had little effect on the rate. To illustrate the method of measuring k_2, some typical data are given in Table Va.

The results summarized in Table V clearly show that at essentially constant P_H (and ionic strength) the rate of furfural semicarbazone formation may be increased five-fold by a change in concentration of the acetate

TABLE Va

DATA ILLUSTRATING METHOD OF MEASUREMENT OF CONDENSATION RATE BETWEEN FURFURAL AND SEMICARBAZIDE

P_H, 4.42; total molarity of acetate + acetic acid, 0.0302; ionic strength, 0.694; temperature, 25.00 ± 0.01°; initial concentration of semicarbazide (x_0), 0.0001811 *M*; initial concentration of furfural ($x_0 + c$), 0.0002332; c = 0.0000521.

Minutes	Cc. of 0.0209-*N* iodine for 20.48-cc. sample	x	k
3.33	3.48	0.0001823	..
14.50	3.23	.0001691	21.3
21.25	3.10	.0001624	23.2
29.75	2.99	.0001566	22.4
37.50	2.87	.0001502	23.2
		Average	22.5

$$kt = 44195 \log \frac{0.7767x + 0.0000405}{x}$$

ion and acetic acid. The increase in rate with increase in concentration is nearly linear up to a molarity of about 0.13; in higher concentrations the increase of concentration produces a less effect. From these results it seemed probable that we were dealing with a reaction between the free semicarbazide (BNH_2) and the carbonyl compound, the reaction being subject to acid catalysis by the acetic acid molecules; as will be shown later, we could obtain no evidence that the reaction was subject to basic catalysis in aqueous solutions. Further evidence was obtained by studying the rate of formation of acetone semicarbazone at 0° in acetate and phosphate buffer solutions. The results are shown graphically in Fig. 2. Since the hydrolysis constant of acetone semicarbazone is high, k_2 was determined indirectly by measurements of the equilibrium constant and of the velocity of hydrolysis of the semicarbazone.

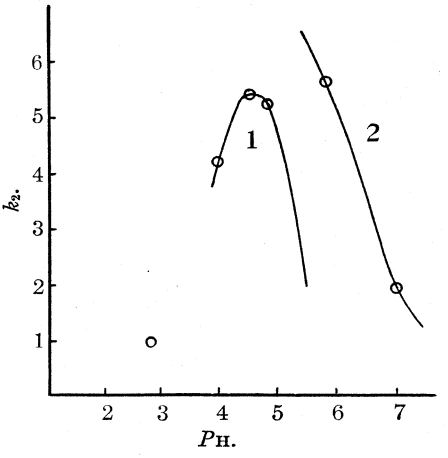


Fig. 2.—Velocity of condensation of acetone and semicarbazide at 0° in 0.045 *M* buffer solutions; curve 1, acetate buffers; curve 2, phosphate buffers.

A test of the applicability of Brönsted's theory to semicarbazone formation is afforded by the results shown in Fig. 2. From the relationship $pK - pH = \log([BNH_3^+]/[BNH_2])$ and the value of pK at 0° for semicarbazide acid ion (4.40),[2] the fraction of total semicarbazide present as free base may be calculated. The reaction velocity constant referred to free semicarbazide ($k_2°$) is obviously the ob-

served velocity constant (k_2) divided by this fraction; this value is given in the fourth column of Table VI.

TABLE VI

SUMMARY OF DETERMINATIONS OF CONDENSATION VELOCITY OF ACETONE AND SEMICARBAZIDE AT 0.1 ± 0.1°

P_H	C_A	k_2	$k_2°$	$k_A = k_2°/C_A$	
2.84	0.0226	1.13	42.2	...	Citric acid buffer
4.00	.0363	4.25	14.9	410	Acetic acid buffers
4.52	.0233	5.43	9.55	406	
4.84	.0157	5.30	7.05	450	
5.84	.0350	5.70	5.90	169	Phosphate buffers
7.00	.0146	2.02	2.02	138	

In the second column of the same table is given the molar concentration of acid in each of the buffers; according to Brönsted's theory the value of $k_2°$ should be proportional to this concentration since in general $k_2° = \Sigma C_A k_A$ where C_A and k_A are the concentrations and specific catalytic constants for all the species of acids involved. The last column in Table VI shows that the value of k_A for acetic acid is 420 ± 5% and for $H_2PO_4^-$, 150 ± 10%. These facts show clearly that the formation of acetone semicarbazone is a reaction involving acetone and free semicarbazide subject to acid catalysis. (No attempt was made to calculate a value for the citric acid buffer since it is difficult to identify the molecular species of acid present in this case.)

Since in general the specific catalytic constants of a series of acids parallel the dissociation constants,[7] it is evident that as one passes from a set of buffers composed of the monobasic phosphate ion to one composed of acetic acid and then to those containing still stronger acids the value of k_A would increase. Furthermore, in a given set of buffers C_A, the concentration of the acid component, increases with decreasing P_H values. These two effects by themselves would cause an increase in the rate of semicarbazone formation with increasing acidity. However, this effect is counteracted by increasing removal of free semicarbazide by the formation of the ion $NH_2CONHNH_3^+$ as soon as one approaches a P_H value near the pK value of the semicarbazide ion. The result of these two opposing factors would obviously lead to a maximum in the P_H versus k_2 curve for semicarbazone formation. It would be clearly accidental, however, if such a curve were a smooth continuous curve; indeed, it is not as shown by Fig. 2. It would be easy, however, to assume that there was such a smooth curve showing a maximum if a limited number of buffer solutions of approximately the same concentration were employed. This is shown by the results we obtained early in the work using furfural at 25°. These measurements are summarized in Fig. 3; the values of k_2 and K were measured directly as explained above. There is a maximum value

of k_2 at P_H 3.13, but the curve is not regular. Ölander obtained a similar maximum in studying acetoxime formation but explained it by an entirely different mechanism. As his measurements were made before Brönsted's work had shown the importance of general acid catalysis, he made no experiments to determine whether or not the P_H value of the solution alone determined the rate. We believe that these results of Ölander's indicate that oxime formation like semicarbazone formation is a reaction between the free base and the carbonyl compound catalyzed by the acid component of the buffer.

The temperature coefficient of the reaction between acetone and semicarbazide was determined at P_H 7 (phosphate buffer molarity of 0.049) by measuring the rate at 0.1 ± 0.1°, and 25.00 ± 0.01°. The values for k_2 were 2.02 ± 0.06 and 2.95 ± 0.06, respectively; these values in the usual Arrhenius equation yield a value for the heat of activation of 2500 cal. ± 240 cal. This, combined with the value of ΔH for the hydrolysis of acetone semicarbazone given above (9700), gives the heat of activation of the hydrolysis reaction as 12,200 cal.

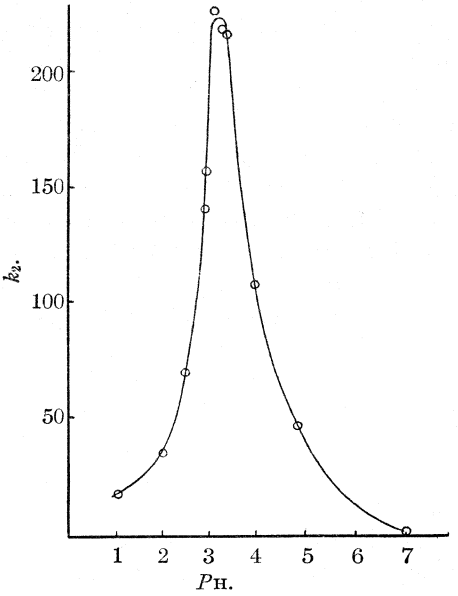


Fig. 3.—Condensation velocity of furfural and semicarbazide in 0.5 *M* phosphate, citrate and acetate buffers.

This latter value is about what one might expect for a reaction of this sort, but the very small heat of activation of semicarbazone formation is very unusual. The facts concerning acid catalysis, however, show that the rate of the reaction is dependent on the concentration of three substances, namely, the carbonyl compound, the reagent and the acid. It seems probable that in reality we have a bimolecular reaction between one of the reactants and a complex of the other two. The low temperature coefficient of the reaction would be accounted for by the fact that the equilibrium involving the complex would be shifted toward dissociation by increased temperature. This shift would diminish the concentration of the reactant in the rate-determining step and lower the velocity. This effect would offset to a considerable extent the usual increase in rate of a reaction with increase in temperature. According to this view, then, the value of the heat of activation of the reaction in question does not correspond to any real reaction but is complicated by including the heat of dissociation of a complex.

We have not been able to obtain any clear evidence of basic catalysis of semicarbazone formation. For study in a borate buffer of P_H 9.11 and a dibasic–tribasic phosphate buffer of P_H 11.01, the most reactive carbonyl compound, acetaldehyde, was chosen. This aldehyde, which condenses with semicarbazide with a velocity constant of about 360 in a 0.1 *M* phosphate buffer at P_H 7, showed a constant of 9.2 in the P_H 9 buffer and a constant of 1.42 at P_H 11. Evidently the rate at neutrality was almost entirely due to catalysis by the $H_2PO_4^-$ ion. Certainly there is no basic catalysis evident by the $PO_4^{\equiv}$ ion in 0.25 *M* solution. To avoid using acetaldehyde, with its tendency to polymerize in strongly basic solutions, cyclohexanone was condensed with semicarbazide in the P_H 11 buffer, and in 0.1 *N* and 1 *N* sodium hydroxide solution, carrying the P_H almost up to 14. The constants, which were not very satisfactory for the slower reactions, were: at P_H = 11.0, k_2 = 0.27 ± 0.06; 0.1 *N* NaOH, k_2 = 0.22 ± 0.03; 1 *N* NaOH, k_2 = 1.61 ± 0.05. There appears to be about a five-fold increase in velocity on passing from 0.1 *N* sodium hydroxide to 1 *N*, which is perhaps too large a difference to be caused by a solvent effect; but since the velocity in normal sodium hydroxide is less than one-twentieth of that in our P_H 7 buffer (with 0.03 *M* monobasic sodium phosphate functioning as an acid catalyst), it would appear that, if there is any basic catalysis of semicarbazone formation, it is exceedingly small in aqueous solutions.

On the other hand, the accelerating effect of strong alkali on oxime formation appears well-established. It was first noticed by Auwers in 1889 and is commonly used in the preparation of the slowly forming oximes of highly substituted ketones. According to the work of Barrett and Lapworth[1b] the velocity of formation of acetoxime increases linearly with the quantity of alkali present, up to an alkali concentration of about 0.025 *N*, which was as high as their experiments were carried. Acree and Johnson put forward the hypothesis that this accelerating effect of alkali on oxime formation was due to formation of the negative ion of hydroxylamine, which had a greater reactivity than the neutral form. If such is the case, we should expect the accelerating effect of alkali on the formation of semicarbazones to be much less pronounced than in the case of oximes, or perhaps not to appear at all in ordinary aqueous solutions, since free semicarbazide shows no acid ionization.

III. The Effect of the Structure of the Carbonyl Compound on the Equilibrium and the Rate

From the work reported in the two previous sections of this paper it is clear that a comparison of rates and equilibria with a variety of carbonyl compounds and the same nitrogen base should be made (a) under conditions where all the nitrogen base and all the condensation product are in

the free-base form, and (b) with a definite concentration of a known catalyst present. This concentration of catalyst should not much exceed 0.1 *M* and should not be more than about 100 times the concentration of the reactants. These conditions will be fulfilled for semicarbazone formation if we choose a phosphate buffer of concentration 0.1 *M* or 0.2 *M* and with a value of P_H 7, since the concentration of the catalyst (primary phosphate ion) in a 0.2 *M* buffer of this P_H is only 0.06 *M*, and since here more than 0.999 of the semicarbazide is in the form of the free base.

In addition to the methods outlined above for measuring equilibrium and rate constants, another method was introduced for convenient determination of the rate of hydrolysis of a semicarbazone. This method is applicable in certain cases only, and depends upon the stability of the semicarbazone toward iodine. If iodine does not attack a semicarbazone directly, hydrolysis may be carried on in a solution containing iodine, and the continuous removal of the semicarbazide by the iodine makes the hydrolysis kinetically irreversible and easily subject to treatment by the simple monomolecular formula.

The constancy of the values of k calculated from any such hydrolysis run where only a slight excess of iodine is present constitutes a sufficient criterion of the stability of the semicarbazone; for if iodine participates in the rate-controlling reaction, the "monomolecular constants" will decrease with time, and be proportional to the concentration of iodine remaining.

The logarithm of the semicarbazone concentration was plotted against the time for the several semicarbazones measured. The method was applied only to those semicarbazones for which such a plot resulted in a straight line; these were acetone, acetaldehyde and cyclohexanone semicarbazones. With the last two, the rate of hydrolysis could be measured more accurately than the rate of formation, so that this was a very useful method in these cases.

An account of the determination of the hydrolysis velocity of acetone semicarbazone will illustrate the method. The dry semicarbazone was weighed and a solution of it in water made up to be about 0.01 *M*. This was kept overnight and then for a few hours in the thermostat; 5-cc. portions of this solution were then introduced into flasks containing 7 cc. of iodine and 20 cc. of a 0.2 *M* phosphate buffer of P_H 7.02. The time from addition of this sample to the iodine, to reaching the end-point with thiosulfate was taken with a stop watch. At any time a new point on any part of the curve could be taken. In another run 50 cc. of 0.1 *M* buffer (P_H 7.08) was used instead of 20 cc. of the 0.2 *M* buffer. This made a buffer concentration of 0.0794 instead of 0.125 and a semicarbazone concentration of 0.00082 instead of 0.001568. The two values for k_1 found are 0.0214 and 0.0152. Corrected to a concentration of catalyst of 0.06 *M* (buffer concentration of exactly 0.1 *M*) these yield the constants 0.017 and 0.019.

The average of these values, divided by the rate of formation of acetone semicarbazone at the same concentration of buffer, ($2.95/0.049 \times 0.100 = 6.0$), gives a value for the equilibrium constant of 0.0030 as compared with 0.00324 from the measurements of equilibrium as a function of P_H (Table I).

In preparing to study the other semicarbazones, blanks were run in each case to test for any reaction between iodine and the ketone or aldehyde itself. In all these cases it was found that there was no reaction rapid enough to be a source of error. Acetaldehyde, for example, reacted forty times more slowly with iodine at P_H 7 than the semicarbazone.

The final results of the comparative study of eight different aldehydes and ketones are given in Table VII.

TABLE VII

COMPARISON OF EQUILIBRIA AND RATES OF SEMICARBAZONE FORMATION OF A VARIETY OF KETONES AND ALDEHYDES

At 25 ± 0.01° in 0.07 *M* Na_2HPO_4 + 0.03 *M* NaH_2PO_4

Semicarbazone of:	$K_{\infty B} \times 10^5$ Hydrolysis constant of semicarbazone	$pK_{\infty B}$	Velocity constants formation = k	Velocity constants hydrolysis $k_1 \times 10^5$
Acetaldehyde	2.9	4.5	(361)	1040
Benzaldehyde	(0.30)	5.5	2.05	(0.62)
Furfural	(0.76)	5.1	0.73	(0.55)
Trimethylacetaldehyde	1.85	4.7	20	(37)
Pyruvic acid	0.51	5.3	7.37	(3.8)
Acetone	324	2.5	6.02	1800
Cyclohexanone	214	2.7	(36)	7600
Pinacolone	1260	1.9	0.068	(86)

In this table the figures which were not determined directly, but were computed from other data at hand, are enclosed in parentheses. The values of $K_{\infty B}$ for benzaldehyde and furfural were calculated by equations 5 and 6 from values of K at different P_H values. Values of k_2 for acetaldehyde and cyclohexanone were calculated from $K_{\infty B}$ and k_1 and the reverse procedure was used in calculating k_1 for the four bracketed values.

A consideration of Table VII brings out a number of points of interest. In the first place it is clear that there is no apparent relation between the speed of formation of the semicarbazone and its stability as measured by the hydrolysis constant $K_{\infty B}$. Thus the rates of formation of the semicarbazones of benzaldehyde, pyruvic acid, trimethylacetaldehyde and acetone are within a power of ten but the hydrolysis constants show a divergence of a thousand-fold between the extremes, and the most rapidly reacting of the four (trimethylacetaldehyde) is about in the middle of the series from the point of view of the extent of hydrolysis of the semicarbazones. Considering first the relation between structure and rate of semicarbazone formation, acetaldehyde is found at the top of the list, with its

trimethyl substitution product about a tenth as reactive, but some ten times more reactive than benzaldehyde or furfural. The latter is the least reactive of all the aldehydes and differs from acetaldehyde by nearly a thousand-fold. Of the ketones, cyclohexanone is the most reactive, as would have been expected from previous work, acetone and pyruvic acid essentially equal and about a sixth as rapid in semicarbazone formation as the cyclic ketone. The large drop in reactivity caused by substitution of three methyl groups (0.068 for pinacolone compared with 6.0 for acetone) is in accord with a large variety of qualitative and quantitative facts of organic chemistry. It is interesting that the change in reactivity produced by the substitution of three methyl groups in the alpha position is much less in the case of the aldehyde than with the ketone (361/20 = 18, compared with 6.0/0.06 = 100). A comparison of benzaldehyde, furfural, acetone and trimethylacetaldehyde gives very little support to the idea that the rate of carbonyl reactions is determined solely by so-called "steric effects." If the comparison is sufficiently restricted, however, as, for example, between acetaldehyde and its trimethyl derivative, the concept of steric hindrance is in accord with the facts.

Turning now to the equilibrium constants, we find all the ketones (except pyruvic acid) falling into one class and the aldehydes into another. Within the ketone class the variation in $K_{\infty B}$ is only three-fold, the most highly substituted ketone being the most completely hydrolyzed. The variation among the aldehydes in $K_{\infty B}$ is ten-fold, but the difference between the least hydrolyzed ketone semicarbazone (always excepting pyruvic acid) and the most hydrolyzed aldehyde semicarbazone is 100-fold. Pyruvic acid behaves like an aldehyde in respect to the hydrolysis constant of the semicarbazone. It would appear that the carbonyl compounds, as far as the energy relationships are concerned, show a rather simple relationship between structure and semicarbazone formation, the equilibrium constant being determined by the same sort of factors which determine the dissociation constants of acids. For convenience these factors may be termed the polarity or negativity of the attached groups.

Using the dissociation constants of the acid XCOOH, as a measure of the negativity of the group X, we have the following series, the groups being arranged in order of decreasing negativity (the values of pK_A for the acids are given in parentheses): COOH (2.8), H (3.7), C_6H_5 (4.2), CH_3 (4.7), $(CH_3)_3C$ (5.0). Now turning to a comparison of the extent of hydrolysis of the semicarbazones formed from carbonyl compounds of the type $XCOCH_3$, we find the following order for the group X (the values of $pK_{\infty B}$ are given in parentheses): COOH (5.3), H (4.5), CH_3 (2.5), $(CH_3)_3C$ (1.9). The two series coincide not only qualitatively but semi-quantitatively, the most hydrolyzed semicarbazone corresponding to the weakest negative group. If we compare the values of pK_B for semicar-

bazones derived from compounds of the type XCHO, we find that the value for benzaldehyde is greater than for acetaldehyde, as would be predicted, but that trimethylacetaldehyde is out of place. This discrepancy we do not feel is serious in view of the uncertainty of the interpretation of small differences in pK values.

We are aware that some of our conclusions in regard to the relation between structure and rate of reaction are contradictory to earlier measurements which have been much quoted. It would take far too much space to discuss all the earlier work but with the exceptions previously noted we feel that the previous work is unreliable because of the then unknown factors affecting both equilibrium and rates and a failure to distinguish between equilibria and rates in the measurements themselves. Furthermore, we have devised a few qualitative experiments which demonstrate the correctness of some of the conclusions summarized in Table VII.

A comparison of semicarbazone formation of cyclohexanone and furfural is of interest. The differences in rate are in favor of the former by a factor of about 50; the hydrolysis of the aldehyde semicarbazone, however, is only 1/300 of that of the ketone. As a result, if one mole of semicarbazide and one mole each of cyclohexanone and furfural are allowed to react, practically the entire *final* product is furfural semicarbazone. Because of the differences in the rates of reaction, however, the *initial* product in such an experiment is almost wholly cyclohexanone semicarbazone. The effects of differences of rate and equilibrium constants on the nature of the product can be shown very simply by allowing semicarbazide to react with a mixture of cyclohexanone and furfural in alcoholic solution and isolating the semicarbazone after a few seconds and after a few hours. Because of the solubility of cyclohexanone semicarbazone in water, it is necessary to precipitate the product by pouring a sample of the mixture into a saturated ammonium sulfate solution in which the cyclohexanone semicarbazone is almost insoluble. In such an experiment starting with 0.01 mole each of semicarbazide hydrochloride, furfural, and cyclohexanone and 0.05 mole of potassium acetate in 50% alcohol, a sample precipitated after twenty seconds yielded a product melting at 165° (identified as cyclohexanone semicarbazone by mixed melting point); after two and one-half hours a similar precipitate melted at 190° and was identified as furfural semicarbazone. In a comparison of acetone and furfural, it is impossible to isolate the ketone semicarbazone by precipitation as it is too soluble. The delayed precipitation of furfural semicarbazone from a reaction mixture containing one mole of acetone (and saturated with furfural semicarbazone) was however striking proof of the correctness of the results shown in Table VII, where k_2 for acetone is nearly ten times greater than that of furfural. Two exactly parallel experiments were performed using an aqueous solution of semicarbazide hydrochloride (0.01 mole) and potassium acetate (0.05 mole) in

20 cc. of water saturated with furfural semicarbazone. In one flask a mixture of 0.01 mole each of acetone and furfural was introduced, in the other 0.01 mole of furfural alone. In the first flask the precipitate after one minute was 0.25 g., in the other 1.20; the filtrate from these precipitates yielded, after standing for twelve hours, 1.00 g. and 0.20 g. of additional furfural semicarbazone.

TABLE VIII

COMPOSITION OF BUFFER SOLUTIONS

*P*H	Acid	Concentration	Salt	Concentration
−0.01	HCl	1.284		
0.50	HCl	...		
1.00	H_3PO_4	0.455	NaH_2PO_4	0.045
1.48	H_3PO_4	.295	NaH_2PO_4	.205
2.02	H_3PO_4	.155	NaH_2PO_4	.345
2.45	H_3PO_4	.425	NaH_2PO_4	.075
2.84	Citric	.25	Sodium citrate	.25
2.87	Citric	.25	(Monobasic)	.25
3.40	Citric	.085	Sodium citrate	.415
3.95	Acetic	.40	Sodium acetate	.10
4.00	Acetic	.40	Sodium acetate	.10
4.52	Acetic	.26	Sodium acetate	.24
4.84	Acetic	.175	Sodium acetate	.325
5.84	NaH_2PO_4	.39	Na_2HPO_4	.11
7.00	NaH_2PO_4	.06	Na_2HPO_4	.14
7.02	NaH_2PO_4	.06	Na_2HPO_4	.14
9.11	Boric	.28	Sodium borate	.22
11.01	Na_2HPO_4	.25	Na_3PO_4	.25

The buffers of other *P*H's in the neighborhood of 3, not listed here, were prepared from these buffers by adding different amounts of acid or base, account being taken of the changes in concentration in the values reported for μ.

Summary

A quantitative study has been made of the factors affecting the equilibria and rates of semicarbazone formation. The extent of hydrolysis of a given semicarbazone is a function of the acidity of the solution, which may be expressed by an equation which has been derived. The results obtained correspond to this equation. The formation of semicarbazones has been found to be subject to general acid catalysis and a fairly satisfactory formulation has been developed in terms of the effect of acidity on the amount of semicarbazide reacting and acid catalysis. The equilibria and rates of semicarbazone formation for a variety of ketones and aldehydes have been measured under strictly comparable conditions. Certain relations between structure and equilibria and rates of semicarbazone formation have been pointed out.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF THE TECHNICAL UNIVERSITY OF FINLAND]

A CONTRIBUTION TO THE CHEMISTRY OF DIHYDRORETENE[1]

BY GUST. KOMPPA AND HARALD P. FOGELBERG

RECEIVED FEBRUARY 18, 1932 PUBLISHED JULY 6, 1932

Introduction and Historical

Retene is a hydrocarbon, 1-methyl-7-isopropylphenanthrene, derived from pine tar. The hydrogenated derivatives of retene are of interest especially because of their relationship to resin acids and in view of their occurrence with retene in pine tar and pine oils.

Dihydroretene may be obtained as a well-characterized, crystalline material by carefully reducing retene with sodium and amyl alcohol. Virtanen,[2] who first isolated dihydroretene by this method, found that the compound, unlike retene, formed no picrate and that it yielded retenequinone on chromic acid oxidation.

It is well known that phenanthrene is more closely related to diphenyl in its chemical behavior than to naphthalene. This property is clearly evident in a series of reactions of phenanthrene in which the double bond of the 9,10 position, the "bridge," appears almost olefinic in nature. It is to be expected that the middle ring of the retene molecule should have the same character as that of phenanthrene. A ring system obtained by saturating the "bridge" double bond of retene should in many respects bear a close relationship to the mother substance, although it is to be expected that the aromatic character of the other two benzene nuclei should be enhanced.

Monosubstitution derivatives of retene have been prepared by halogenation, carboxylation and sulfonation.[3] Of these, the last mentioned are the best characterized. Komppa and Wahlforss[4] isolated two monosulfonic acids and from them prepared a series of well-characterized derivatives. These sulfonic acids, designated as A-retenesulfonic acid and B-retenesulfonic acid, are colorless, crystalline substances free of water of crystallization and possess sharp melting points.[5] In view of these

[1] Abstracted from a thesis presented by Harald P. Fogelberg in October, 1925, to the chemistry faculty of the Technical University of Finland in partial fulfilment of the requirements for the Doctorate. Acknowledgment is made to Dr. L. A. Goldblatt, University of Pittsburgh, Pittsburgh, Pa., and Dr. Eric Wahlforss, Hammermill Paper Company, Erie, Pa., in appreciation of the assistance rendered in abstracting this paper from the original thesis.

[2] Virtanen, *Ber.*, **53**, 1880 (1920).

[3] Additional derivatives of retene have recently been reported by Bogert and Hasselström, THIS JOURNAL, **53**, 3462 (1931), and by Fieser and Young, *ibid.*, **53**, 4120 (1931). (Abstractors' note.)

[4] Komppa and Wahlforss, *ibid.*, **52**, 5009 (1930).

[5] Fieser and Young suggest that the A- and B-substituents occupy the 2- and 6-positions, respectively, in retene. In this connection they state: "While no promising

circumstances it seemed desirable to study similar reactions of dihydroretene.

Results and Discussion

The sulfonation of dihydroretene gave, in good yields, two monosulfonic acids. Sulfonation at 66° resulted in the formation of a monosulfonic acid which was characterized by its difficultly soluble alkali salts. The acid, purified by means of its barium salt, when recrystallized from ether melted at 147–148°. Sulfonation at 200° resulted in the formation of a second monosulfonic acid which, when regenerated from its ethyl ester and recrystallized from benzene, melted at 106–107°. The sulfonic acid group could be eliminated from the former much more easily than from the latter. Dihydroretene could readily be regenerated from the sulfonic acid melting at 147–148° by heating with water at 200°. On the other hand, the products obtained by treating the sulfonic acid melting at 106–107° either with water or with concentrated hydrochloric acid, could not be definitely identified as dihydroretene.

Fusion of the alkali salts of the two monosulfonic acids with potassium hydroxide gave, in very low yields, two phenols. They were found to be identical with the retenols obtained from retene by Komppa and Wahlforss.[4] This was established by preparing the acetyl and benzoyl derivatives of the phenols obtained from both hydrocarbons. This result indicated that dehydrogenation had occurred and implied that the sulfonic acid groups in the sulfonic acids of retene and dihydroretene were in analogous positions. In order to obtain further evidence the ethyl esters of A- and B-retenesulfonic acids were prepared and oxidized with chromic acid to the ethyl esters of retenequinonesulfonic acid. The ethyl esters of the two dihydroretenesulfonic acids were similarly oxidized. The quinonesulfonic ester thus obtained from the dihydroretenesulfonic acid melting at 147–148° was identified, by melting point and the mixed melting point test as well as other characteristics, as the ethyl ester of A-retenequinonesulfonic acid. On the other hand, the properties of the quinonesulfonic acid ester obtained from the dihydroretenesulfonic acid melting at 106–107° corresponded to those of the ester of B-retenequinonesulfonic acid. This shows, consequently, that in the sulfonation of dihydroretene the substituents enter positions analogous to those in A- and B-retenesulfonic acid. The new sulfonic acids were, therefore, designated as A-dihydroretenesulfonic acid and B-dihydroretenesulfonic acid. The addition of two hydrogen atoms has, therefore, apparently not changed the behavior of the retene nucleus toward substitution reactions.

method of degradation was discovered, we believe that, from certain properties of the compounds in the two series, the two retenols may be assigned structures which, if not definitely proved, are highly probable." (Abstractors' note.)

The acid chloride as well as the methyl and ethyl esters of both dihydroretenesulfonic acids were prepared. The acid chloride of A-dihydroretenesulfonic acid was reduced to the corresponding sulfinic acid and to the mercaptan.

During the course of this research it was found necessary to prepare a number of derivatives of retene. The description of the preparation of these compounds constitutes the last portion of the Experimental Part.

The following is a comparison of the derivatives of dihydroretene prepared in this investigation with the corresponding derivatives of retene.

TABLE I

Substituent	Dihydroretene derivatives, °C. A-	B-	Retene derivatives, °C. A-	B-
—$SO_2OH + 2H_2O$	147–148	106–107		
—SO_2OH			188–189[4]	121–123[4]
—SO_2Cl	91–92(82–83)	112–113	135–136	146.5–148[4]
—SO_2NH_2	193–194	189–190		206–207.5[4]
—$SO_2NHC_6H_5$	112–114	196–197		
—SO_2OCH_3	98–99	85– 86	164–166[4]	117–119[4]
—$SO_2OC_2H_5$	72.5–73.5	78– 79	137.5–138.5	114–115
Ditto quinone	183–184	169–171	183–184	170–170.5
—SO_2H	123–130			
—SH	185–188			
—$SCOC_6H_5$	170–172			
—OH			200–202[4]	158–159[4]
—$OCOCH_3$			160[3]	132–134[4]
—$OCOC_6H_5$			177–178	112
—OCH_3			147–148	115–116[3]

Frey[6] obtained a mixture of diphenyl ketone and potassium phenanthrenesulfonate by boiling the potassium salt of phenanthrenequinonesulfonic acid with aqueous potassium hydroxide. In order to determine whether the corresponding reaction occurred with retene derivatives, the potassium salts of A- and B-retenequinonesulfonic acids were boiled with aqueous potassium hydroxide. Potassium retenesulfonate, however, could not be identified among the products of the reaction. A mixture containing the potassium salt of a retene ketone monosulfonic acid was obtained from A-retenequinonesulfonic acid while retene ketone was the principal product from B-retenequinonesulfonic acid.

From the highest boiling fractions of pine tar (from *Pinus Sylvestris*) used as a raw material in this investigation, there was isolated a small amount of another, apparently new, hydrocarbon, possessing the formula $C_{24}H_{20}$.

Experimental Part

The retene used in these experiments was obtained from that fraction of pine tar boiling at about 360°. Besides retene, a small quantity (less than 1 g. from 500 g. of

[6] Werner, *Ann.*, **321**, 345 (1902).

crude retene) of another hydrocarbon was isolated from this crude material in the course of recrystallization from petroleum ether. This substance crystallized from benzene in shining silver scales melting at 297–298° (uncorr.). This hydrocarbon was quite difficultly soluble in most solvents and appeared to be sulfonated by hot concentrated sulfuric acid. Analysis indicated the formula $C_{24}H_{20}$ for this hydrocarbon.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54; mol. wt. 308.16. Found: C, 93.68, 93.83; H, 6.52, 6.35; mol. wt. (Rast),[7] 306, 311.

Dihydroretene.—This compound was prepared essentially according to the method described by Virtanen.[2] The total yield of dihydroretene, m. p. 64–65°, amounted to 62.7% of the theoretical.

Dihydroretene Derivatives A-Series

A-Dihydroretenesulfonic Acid.—To 20 g. of dihydroretene heated on an oil-bath to 66–68° was added, with vigorous stirring, 20 g. of sulfuric acid (sp. gr. 1.84). The sulfonation was completed in fifteen minutes. The sulfonation mixture was then poured into 200 cc. of hot water and thoroughly agitated. Under these conditions the sirupy mass dissolved, forming a quite clear bright yellow solution. The ammonium salt of A-dihydroretenesulfonic acid precipitated immediately upon the addition of an excess of concentrated ammonium hydroxide. After standing overnight the salt was filtered off, washed with cold water and dried at 110°. The dried product was extracted with petroleum ether (b. p. 80–100°) in a Soxhlet extractor; yield 19.5 g. (69.1%).

The ammonium salt (10 g.) was dissolved in 150 cc. of a mixture of equal parts of pyridine and water. The solution was filtered and a warm aqueous solution of barium chloride was stirred in. The barium salt of the sulfonic acid which precipitated was filtered off, washed repeatedly with hot water and dried.

Of the barium salt obtained in this way, 11.5 g. was warmed and stirred with 80 cc. of glacial acetic acid until a homogeneous thin paste was obtained. Then 45 cc. of sulfuric acid (2 *N*) was gradually added and the mixture was heated nearly to boiling for ten minutes. Warm water (35 cc.) was then added and the solution filtered through a hot water funnel. The quite clear yellowish filtrate was concentrated *in vacuo* to about 75 cc. and 10 cc. of dilute sulfuric acid (1:1) added. On cooling the liquid solidified to a stiff white paste which could easily be filtered by suction. The shining scales of the sulfonic acid thus obtained were spread out on a porous plate. The acetic acid could be removed, almost completely, by allowing the product to stand over concentrated sodium hydroxide solution in a vacuum desiccator; yield, 7.6 g. The acid was obtained in the form of strongly refracting crystals melting at 147–148° by recrystallization from ether. The acid was titrated in aqueous alcohol solution with *N*/10 aqueous sodium hydroxide: calcd. for 0.1701 g. of $C_{18}H_{19}SO_3H + 2H_2O$: 4.83 cc.; found: 4.85 cc.

The acid lost its water of crystallization on standing over sulfuric acid in a vacuum desiccator.

Salts.—A number of salts of A-dihydroretenesulfonic acid were prepared and analyzed.

Methyl Ester.—Prepared by boiling the potassium salt with dimethyl sulfate for four minutes. Recrystallization from methyl alcohol gave slightly yellowish scales, m. p. 98–99°.

Anal. Calcd. for $C_{19}H_{22}SO_3$: C, 69.04; H, 6.71. Found: C, 68.81; H, 6.70.

Ethyl Ester.—Prepared by boiling the potassium salt with diethyl sulfate. Recrystallization from ethyl alcohol gave fine scales, m. p. 72.5–73.5°.

Anal. Calcd. for $C_{20}H_{24}SO_3$: C, 69.71; H, 7.03. Found: C, 69.18, 69.52; H, 7.06, 6.81.

[7] Rast, *Ber.*, **55**, 1051 (1922).

TABLE II

Salt	H_2O of crystallization	Crystallized as	Dried at °C.	Solubility[d]	Analyses, anhydrous salt, % Calcd.	Found
Na[a]	H_2O	Shiny scales	110	0.040	Na, 6.80	6.74
K[b]	H_2O	Thin prisms	110	.048	K, 11.04	10.87
NH_4[a]		Crystalline powder	110	.057	N, 4.20	4.10 (Kjeldahl)
Ba[a]		Crystalline powder	150	.0025	Ba, 17.89	17.79
Ca[a]		Crystalline powder	150	.005	Ca, 5.98	6.05
Cu[b]	$2H_2O$	Light green blue scales	150[c]	.011	Cu, 9.16	8.84

[a] Prepared from the free acid and the metallic hydroxide. [b] Prepared from the free acid and the metallic carbonate. [c] Lost its water of crystallization at 110°. [d] Grams of anhydrous salt per 100 g. of water at 17°.

To a solution of two grams of the ethyl ester in 50 cc. of glacial acetic acid gently heated on a water-bath was slowly added a warm solution of three grams of chromic acid in 30 cc. of glacial acetic acid. The solution was heated for forty-five minutes, allowed to cool and poured into cold water. The precipitate which formed was filtered off and dried on a porous plate; yield, 0.95 g. (44.0%).

Recrystallization from glacial acetic acid gave small light orange colored needles, m. p. 183–184°. These crystals exhibit complete identity in physical properties and appearance with the product obtained from the oxidation of ethyl A-retenesulfonate. A mixed melting point test of the two oxidation products showed no depression of the melting point. The substance was difficultly combustible.

Anal. Calcd. for $C_{20}H_{20}SO_5$: C, 64.48; H, 5.42. Found: C, 64.57, 63.24, 62.85; H, 6.00, 5.96, 6.66.

Chloride.—Prepared by treating potassium A-dihydroretenesulfonate with phosphorus pentachloride in the presence of a small amount of phosphorus oxychloride. The reaction was completed by warming for a short while on a water-bath. After cooling the reaction product was poured into ice water, extracted with ether and the ether solution was washed with water. Evaporation of the ether gave a yellow oil which quickly solidified; yield, 1.8 g. (95.3%). Recrystallization from benzine (b. p. 80–100°) gave thin star-shaped prisms, m. p. 91–92°.

In some cases a second modification of the chloride was obtained. This crystallized from benzine as dense granules which, despite repeated recrystallization, did not melt above 82–83°. Analysis gave values which agreed with those calculated for $C_{19}H_{19}SO_2Cl$. Both chlorides gave an amide, m. p. 193–194°, with ammonium hydroxide.

Anal. (Carius). Calcd. for $C_{18}H_{19}SO_2Cl$: Cl, 10.60; S, 9.58. Found: Cl, 10.41; S, 9.82.

Amide.—Prepared from the chloride of A-dihydroretenesulfonic acid and ammonium hydroxide; yield, 46.6%; colorless scales, m. p. 193–194°.

Anal. Calcd. for $C_{18}H_{21}SO_2N$: N, 4.44. Found: N, 4.49.

Anilide.—Prepared by boiling the chloride of A-dihydroretenesulfonic acid with aniline; yield, 51.3%. The anilide crystallized from alcohol in shining plates, m. p. 112–114°.

Anal. Calcd. for $C_{24}H_{25}SO_2N$: N, 3.58. Found: N, 3.40.

A-Dihydroretenesulfinic Acid.—The chloride of A-dihydroretenesulfonic acid (2 g.) was dissolved in 10 g. of toluene and 2 cc. of water added. The mixture was warmed and shaken on a water-bath while 3 g. of zinc dust was gradually added. A vigorous reaction began and the mass thickened to a stiff paste. Heating and stirring was continued, however, for a short while. After cooling, the mixture of the zinc salt

of the sulfinic acid and unchanged zinc dust was filtered off, washed with a little toluene, and dried. The residue was boiled with a solution of sodium carbonate in aqueous alcohol (1:1) and filtered. On cooling the sodium sulfinate crystallized in shining colorless scales; yield, 1.1 g. (57.1%). The salt is difficultly soluble in water.

Anal. Calcd. for $C_{18}H_{19}SO_2Na$: Na, 7.14. Found: Na, 7.13.

The sulfinic acid was freed from its sodium salt by concd. hydrochloric acid. Crystallization from aqueous alcohol gave white scales, m. p. 123–130°. The acid was titrated with $N/10$ sodium hydroxide: calcd. for 0.1110 g. of $C_{18}H_{19}SO_2H$: 3.70 cc.; found, 3.35 cc.

A-Dihydroretene Mercaptan.—The chloride of A-dihydroretenesulfonic acid was first reduced with zinc dust, giving the zinc sulfinate. This was further reduced in the cold with zinc dust in the presence of concd. hydrochloric acid. The mercaptan was obtained in the form of fine, light yellow scales, m. p. 185–188°; yield, 10.4%. As the substance seemed to be quite unstable, it was converted directly to the benzoyl derivative by means of benzoyl chloride in the presence of pyridine. In this way lemon yellow crystalline granules were obtained, m. p. 170–172°.

Anal. Calcd. for $C_{25}H_{24}SO$: C, 80.59; H, 6.50. Found: C, 80.74; H, 6.68.

Attempted Preparation of A-Dihydroretenol.—All attempts to replace the sulfonic acid group of potassium A-dihydroretenesulfonate, by means of alkali fusions, with the hydroxy group resulted in the formation of A-retenol. The yields were uniformly low; 15.6% from a fusion carried out in the usual manner. The retenol crystallized from xylene in the form of small glistening plates, m. p. 200–202°. With picric acid the picrate, m. p. 150–151°, was obtained in the form of ruby red needles.

Dihydroretene Derivatives, B-Series

B-Dihydroretenesulfonic Acid.—To 10 g. of dihydroretene heated on an oil-bath to 200° was added, with vigorous stirring, 10 g. of sulfuric acid (sp. gr. 1.84). The sulfonation was completed in five minutes. The sulfonation mixture was poured into 150 cc. of hot water and a slight excess of concentrated ammonium hydroxide was added to the hot solution. After standing overnight, 1.6 g. of a crystalline salt precipitated out. This was filtered off and the cloudy filtrate was extracted with ether. The clear aqueous solution was heated on a water-bath to remove the ether and then treated with a solution of 10 g. of potassium hydroxide in 30 cc. of water. When cooled, the potassium B-dihydroretenesulfonate crystallized in shining plates; yield, 5.78 g. (36.7%).

The first precipitate obtained with ammonium hydroxide was found to be mostly ammonium B-retenesulfonate.

Potassium B-dihydroretenesulfonate (5 g.) was dissolved in two liters of hot water and acidified with hydrochloric acid. An excess of barium chloride was added and the mixture was boiled for a few minutes. The precipitated barium B-dihydroretenesulfonate was filtered off, washed repeatedly with hot water and boiled for several hours with the calculated quantity of very dilute sulfuric acid. The barium sulfate was filtered off and the clear filtrate was concentrated, first on a water-bath and then *in vacuo* over sulfuric acid. This product, purified by recrystallization from benzene, gave slightly brownish colored scales, m. p. 105–106°, which, air dried, contained two molecules of water; both were lost when dried over sulfuric acid.

The free sulfonic acid was also obtained as nearly colorless scales, m. p. 106–107°, by saponifying the ethyl ester. The acid was titrated with $N/10$ potassium hydroxide: calcd. for 0.11 g. of $C_{18}H_{19}SO_3H + 2H_2O$: 3.12 cc.; found, 3.12 cc.

Salts.—A number of salts of B-dihydroretenesulfonic acid were prepared and analyzed.

TABLE III

Salt	H_2O of crystallization	Crystallized as	Dried at °C.	Solubility[e]	Analysis, anhydrous salt, % Calcd.	Found
K[a]	H_2O	Shiny scales	150[d]	0.248	K, 11.04	10.75
NH_4[b]		Leaflets	110	7.73	N, 4.20	4.28 (Kjeldahl)
Ba[b]	H_2O	Crystalline powder	130	0.026	Ba, 17.89	17.79
Ca[b]	$6H_2O$	Shiny scales	150	0.031	Ca, 5.98	5.82
Cu[c]	$5.5H_2O$	Green-blue needles	150	0.038	Cu, 9.16	8.86

[a] Prepared from the free acid and potassium carbonate. [b] Prepared from the free acid and the metallic hydroxide. [c] Prepared from the ammonium salt and copper chloride. [d] Lost its water of crystallization at 110°. [e] Grams of anhydrous salt per 100 g. of water at 17°.

Methyl Ester.—Prepared by boiling the dried potassium salt with dimethyl sulfate. yield, 50.3%. Recrystallization from methyl alcohol gave small scales, m. p. 85–86°;

Anal. Calcd. for $C_{19}H_{22}SO_3$: C, 69.04; H, 6.71. Found: C, 68.72; H, 6.71.

Ethyl Ester.—Prepared by boiling the dried potassium salt with diethyl sulfate; yield, 82.3%. Recrystallization from ethyl alcohol gave long, colorless prisms, m. p. 78–79°.

Anal. Calcd. for $C_{20}H_{24}SO_3$: C, 69.71; H, 7.03. Found: C, 69.53; H, 7.10.

The ethyl ester was oxidized by chromic acid in a manner similar to that used for the oxidation of the corresponding A-derivative. Orange colored needles were obtained, m. p. 169–171°; yield, 58.5%. The crystals exhibited complete identity in physical properties and appearance with the ethyl B-retenequinonesulfonate obtained by oxidizing ethyl B-retenesulfonate. A mixed melting point test of the two oxidation products showed no depression of the melting point. The substance was difficultly combustible.

Anal. Calcd. for $C_{20}H_{20}SO_5$: C, 64.48; H, 5.42. Found: C, 64.10, 64.18; H, 5.40, 5.56.

Chloride.—Prepared by treating anhydrous potassium B-dihydroretenesulfonate with phosphorus pentachloride in the presence of phosphorus oxychloride, as in the case of the corresponding A-derivative; yield, 74.1%. Recrystallization from benzine gave yellowish, symmetrical crystals, m. p. 112–113°.

Anal. (Carius). Calcd. for $C_{18}H_{19}SO_2Cl$: Cl, 10.60; S, 9.58. Found: Cl, 10.72; S, 9.93.

Amide.—Obtained as small scales, m. p. 189–190°, from the chloride and ammonium hydroxide.

Anal. Calcd. for $C_{18}H_{21}SO_2N$: N, 4.44. Found: N, 4.10.

Anilide.—Prepared in a manner similar to that used for the preparation of the corresponding A-derivative. The anilide crystallized from alcohol in shining scales, m. p. 196–197°.

Anal. Calcd. for $C_{24}H_{25}SO_2N$: N, 3.58. Found: N, 3.58.

Attempted Preparation of B-Dihydroretenol.—All attempts to replace the sulfonic acid group of potassium B-dihydroretenesulfonate, by means of alkali fusions, with the hydroxy group resulted in the formation of B-retenol. The yields were uniformly low, 8.5% from a fusion carried out in the usual manner. After two crystallizations from alcohol–water, slightly yellowish scales of B-retenol, m. p. 158–159°, were obtained. The B-retenol was identified by means of its acetyl and benzoyl derivatives.

Retene Derivatives, A-Series

Ethyl A-Retenesulfonate.—Prepared from ammonium A-retenesulfonate and diethyl sulfate; yield, 61.7%; small, colorless leaflets, m. p. 137.5–138.5°.

Anal. Calcd. for $C_{20}H_{22}SO_3$: C, 70.12; H, 6.48. Found: C, 69.91; H, 6.52.

A-Retenesulfonyl Chloride.—Prepared from ammonium A-retenesulfonate, phosphorus pentachloride and phosphorus oxychloride; yield, 78.6%. Recrystallization from ether gave light yellow scales, m. p. 135–136°.

Anal. (Carius). Calcd. for $C_{18}H_{17}SO_2Cl$: Cl, 10.66; S, 9.64. Found: Cl, 10.52; S, 9.40.

Ethyl A-Retenequinonesulfonate.—Ethyl A-retenesulfonate was oxidized by chromic acid in a manner similar to that used for the oxidation of the corresponding dihydro derivative; yield, 39.4%. When crystallized from glacial acetic acid, small light orange yellow needles, m. p. 183–184°, were obtained. This substance, as was stated previously was identical with the product obtained by oxidizing ethyl A-dihydroretenesulfonate.

Action of Aqueous Potassium Hydroxide on Potassium A-Retenequinonesulfonate.—Potassium A-retenequinonesulfonate (6.8 g.) obtained from A-retenesulfonic acid, was boiled for three hours with about 120 cc. of a 50% solution of potassium hydroxide. The product was cooled and filtered. The residue was washed with water and dried on a porous plate. The light yellow product (5.5 g.) was separated by repeated recrystallization from aqueous alcohol into two fractions.

Fraction 1.—The more easily soluble portion, canary yellow in color, comprised about three-fifths of the original material. Analysis gave values which agreed with those calculated for potassium retene ketone sulfonate. Calcd. for $C_{17}H_{15}O_4SK$: C, 57.58; H, 4.27; K, 11.04. Found: C, 57.53; H, 4.56; K, 10.92. Esterification with diethyl sulfate resulted in the formation of small needles, m. p. 130°, insufficient in quantity for an analysis.

Fraction 2.—The more difficultly soluble portion consisted of an apparently crystalline light yellow powder. Analysis gave no conclusive evidence as to the composition of this product. After fusion with potassium hydroxide an acid which crystallized from benzene in the form of small scales melting at 160° was obtained. Analysis gave values which agreed with those calculated for methyl isopropyl diphenylmonocarboxylic acid. Calcd. for $C_{17}H_{18}O_2$: C, 80.27; H, 7.14. Found: C, 80.00; H, 7.16. The acid was titrated with $N/10$ potassium hydroxide: calcd. for 0.0637 g. $C_{16}H_{17}$-COOH, 2.51 cc.; found, 2.30 cc.

A-Methoxyretene ($CH_3OC_{18}H_{17}$).—Prepared by heating an alcoholic solution of A-retenol and dimethyl sulfate in the presence of sodium hydroxide; yield, 63.1%. Crystallization from alcohol gave colorless needles melting at 147–148°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.31; H, 7.63. Found: C, 86.29; H, 7.78.

A-Benzoxyretene ($C_6H_5COOC_{18}H_{17}$).—Prepared from A-retenol and benzoyl chloride in pyridine solution; yield, 57.4%. When crystallized from alcohol the benzoyl derivative was obtained in the form of tufts of needles, moderately soluble in ether and melting at 177–178°.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.70; H, 6.26. Found: C, 84.84; H, 6.34.

Retene Derivatives, B-Series

Ethyl B-Retenesulfonate.—Prepared from ammonium B-retenesulfonate and diethyl sulfate; yield, 87.1%. Crystallization from alcohol gave small pointed scales, m. p. 114–115°.

Anal. Calcd. for $C_{20}H_{22}SO_3$: C, 70.12; H, 6.48. Found: C, 69.93; H, 6.54.

Ethyl B-Retenequinonesulfonate.—Ethyl B-retenesulfonate was oxidized in glacial acetic acid solution with chromic acid. Recrystallization of the oxidation product from glacial acetic acid gave small, orange colored needles, identical with those obtained by the oxidation of ethyl B-dihydroretenesulfonate, but distinctly darker than those obtained from the corresponding A-derivative.

Action of Aqueous Potassium Hydroxide on Potassium B-Retenequinonesulfonate.—A mixture of 7.6 g. of potassium B-retenequinonesulfonate and 40 cc. of 50% aqueous potassium hydroxide was refluxed for forty-five minutes. After cooling, the insoluble part was filtered off, washed with water and dried on a porous plate. Crystallization from alcohol gave sulfur-yellow flat prisms, m. p. 88–89°. Analysis gave values which agreed with those calculated for retene ketone, $C_{17}H_{16}O$; yield, 3 g. (62.2%). Calcd. for $C_{17}H_{16}O$: C, 86.39; H, 6.83. Found: C, 86.59; H, 6.60. For further identification the substance was reduced in alcohol solution by means of zinc dust in the presence of ammonium hydroxide. The retenefluorenyl alcohol thus obtained as pointed colorless scales, m. p. 132–133°, was analyzed. Calcd. for $C_{17}H_{18}O$: C, 85.66; H, 7.62. Found: C, 86.03; H, 7.41.

B-Benzoxyretene ($C_6H_5COOC_{18}H_{17}$).—Prepared from B-retenol and benzoyl chloride in pyridine solution; yield, 58.8%. Crystallization from alcohol gave well-developed plates, m. p. 112°.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.70; H, 6.26. Found: C, 84.72; H, 6.38.

Summary

The stability and aromatic character of dihydroretene as well as the similarity to retene in behavior has been studied.

Sulfonation gave two well-defined sulfonic acids which were isolated by means of their potassium salts. These were used in the preparation of a number of derivatives. In general they exhibited marked similarity in mode of preparation and in properties with the previously known A- and B-retenesulfonic acids. Oxidation of the ethyl esters of the A- and B-dihydroretenesulfonic acids resulted in the formation of the corresponding ethyl A- and B-retenequinonesulfonates. This showed that the sulfonic acid group had entered similar positions in the two hydrocarbons. Attempts to replace the sulfonic acid group of A- and B-dihydroretenesulfonic acid by the hydroxy group resulted in simultaneous dehydrogenation and consequent formation of the corresponding retenols.

For the purpose of comparison a number of additional derivatives of retene were prepared. The action of boiling aqueous potassium hydroxide on the potassium retenequinonesulfonates was studied. Retene ketone was obtained in good yield from potassium B-retenequinonesulfonate.

A new crystalline hydrocarbon, $C_{24}H_{20}$, m. p. 297–298° (uncorr.), occurring in small quantities with retene in the highest boiling fractions of pine tar, was isolated.

HELSINGFORS, FINLAND

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

DEGREE OF PIGMENTATION AND ITS PROBABLE RELATIONSHIP TO THE MINERAL CONSTITUENTS OF HONEY

BY H. A. SCHUETTE AND KATHORA REMY

RECEIVED FEBRUARY 19, 1932 PUBLISHED JULY 6, 1932

Although honey's chief characteristic does not appear to be the quantity of mineral matter which it contains, yet two reasons suggest themselves why there is need for more information on its inorganic constituents than is now available. One centers around the newer emphasis placed by students of nutrition on the value of manganese and copper in the diet, the other around the present practice in merchandizing this saccharine food which reaches the consumer in its natural state, that is not refined by any manufacturing processes.

It is not required that honey be sold in interstate commerce on the basis of floral source. This is a matter which is left to the discretion of the several states. Rather it must bear a grade in which color, appearance and freedom from generally recognized disagreeable flavors are given predominant consideration. To that end there have been adopted such color designations as *white*, modified when necessary to indicate lighter tints by the words *water* or *extra; amber*, likewise qualified to differentiate the lesser pigmented members of this group by the terms *extra light* or *light;* whereas the adjective *dark* is reserved for the most heavily pigmented honeys.

Although it is perhaps suspected by those conversant with the chemistry of honey that, as between a deeply pigmented product and one less so, the mineral content of the former will in general exceed that of the latter, yet no published reference to this situation has apparently been made heretofore. Be that as it may, however, color and quality often bear an inverse relationship to each other in the lay mind. For this reason it seemed worth while to seek quantitative data in support or contradiction of this circumstance for it would follow, on *a priori* grounds at least, that a deeply pigmented honey ought to be deemed superior to one of light color from the standpoint of nutritive value if the mineral content of the former should prove to be higher. On making an analysis of the ash of twenty-two floral nectar and honey-dew honeys which had been selected at random from widely separated localities in this country in order to reduce any suggestion of accidental results, such was actually found to be the case. This observation in itself is not presented as novel, rather the fact that iron, copper and manganese appear to predominate in the mineral matter of dark honeys.[1]

[1] A line of demarcation has been arbitrarily drawn between the *white* honeys, typified by those from clover or alfalfa and probably indicative of the layman's conception of a light colored product, and the *light amber* honeys as representing the dark

A search of the literature of the past three decades reveals that, although data on the total mineral content of honey are plentiful, yet comparatively few are available with respect to the aforementioned elements.[2-8] Gottfried[2] has already called attention to the probable existence of a relationship between the manganese content and the albuminoids of honey. Lindow and his colleagues[6] in this country and Svoboda in Czechoslovakia are probably among the first to report the presence of copper in this food though unfortunately their records do not reveal a description of the material under examination. Fehlmann[3] found silica in several Swiss honeys and advanced the opinion that its presence there was purely adventitious. Sundberg and Lundgren[7] also reported it as present in the honeys of Swedish origin which they examined. An inspection of their data shows that there is apparently a progression in the silica content of their samples with an increasing depth of color. Existing data for iron[3,4,7,8] with the probable exception of those of Elser[4] and his Swedish contemporaries,[7] do not lend themselves very well to a similar analysis.

Experimental

Material.—With four exceptions (marked by an asterisk in Table I) all samples were obtained in the comb and extracted in the laboratory. As for the others, there was no apparent reason for assuming that they had been extracted in the apiary under conditions leading to the introduction of extraneous metal or mineral matter.

Ashing of Samples.—Weighed amounts of honey in approximately 75-g. portions were first evaporated in large platinum dishes on a hot-plate until substantially all of the water had been driven off. The resulting honey solids were then carbonized over an open flame, after which they were reduced to an ash in an electrically heated muffle furnace whose temperature was kept at a dull redness. The top and sides of the furnace were lined with sheet platinum for the purpose of preventing contamination of the contents of the dishes.

Inasmuch as the determinations of silica were to be made macrochemically it was, therefore, desirable to obtain fairly large mineral residues, and this was only possible by ashing more material than is the usual practice. To that end three to eighteen portions of each honey, depending upon the material available, were separately incinerated, the weight of the respective residues being noted. It was found that the average deviations in the determination of the ash by this mode of procedure lay between ± 0.0008 and $\pm 0.006\%$ for the entire series.

Determination of Silica.—Silica was determined in the usual way, that is, treatment of the ash with 10 cc. of hydrochloric acid (1 + 1), evaporation of the whole to dryness and the addition to the residue of 5 cc. of 1 *N* hydrochloric acid and a like volume of

ones, this group herein being headed by those in which Spanish needle is the predominating floral source.

[2] Gottfried, *Pharm. Zentr.*, **52**, 787 (1911); **53**, 4040 (1912).

[3] Fehlmann, *Schweiz. Bienenztg.*, **48**, 129 (1912).

[4] Elser, *Archiv. Bienenkunde*, **7**, 276 (1926).

[5] Nottbohm, *ibid.*, **8**, 207 (1927).

[6] Lindow, Elvehjem and Peterson, *J. Biol. Chem.*, **82**, 465 (1929).

[7] Sundberg and Lundgren, *Archiv. Bienenkunde*, **11**, 324 (1930).

[8] Svoboda, *Český Včelař*, **64**, 243 (1930).

water, and finally digestion of the mixture for thirty minutes on a water-bath, solution of the soluble constituents in hot water and filtration. The combined filtrates and washings from all the ash portions of each sample were evaporated to dryness, after which the residue was treated as before, the filtrate this time being made up exactly to 100 cc. The silica was volatilized as the tetrafluoride. After corrections were made for the blank on the reagents, a practice which was followed throughout this investigation, the silica content was calculated on the basis of mg. per kilo of honey and per cent. of the ash.

Determination of Iron.—Iron analyses were made colorimetrically by the ferric thiocyanate procedure[9] with application of the technique of Kennedy,[10] who suggested that the reaction product be extracted with amyl alcohol. Aliquots for analysis were chosen to fit the needs of the individual honeys, sample weights lying between 6 and 24 g. representing the limits employed for the whole series. The volume of standard solution which was used for comparison contained 0.04 mg. of iron. Data obtained in the determination of this and the succeeding elements are reported on the same basis as is the silica content.

Determination of Copper.—The Elvehjem and Lindow modification[11] of the potassium thiocyanate–pyridine procedure[12] was used for the determination of copper.

TABLE I

ASH, SILICA, IRON, COPPER AND MANGANESE CONTENT OF LIGHT AND DARK HONEYS

Predominating floral source	Origin	Ash, %	Silica mg. per kg.	Silica % of ash	Iron mg. per kg.	Iron % of ash	Copper mg. per kg.	Copper % of ash	Manganese mg. per kg.	Manganese % of ash
Alfalfa	Colorado	0.039	6.6	1.67	1.2	0.29	0.20	0.05	0.17	0.04
Alfalfa	Wyoming	.043	7.4	1.71	1.5	.36	.35	.08	.18	.04
Clover	Minnesota	.048	8.3	1.72	1.2	.26	.14	.03	.34	.10
Clover	New York	.167	9.7	0.58	3.9	.23	.70	.04	.22	.03
Clover	Wisconsin	.057	7.2	1.23	2.5	.43	.29	.05	.43	.07
Clover	Wisconsin	.040	8.8	2.17	2.1	.52	.30	.08	.38	.09
Clover	Wisconsin	.045	10.2	2.23	2.3	.51	.35	.08	.42	.09
Clover	Wisconsin	.046	9.9	2.12	3.2	.68	.21	.05	.29	.06
Clover	Wisconsin	.083	9.6	1.15	2.1	.25	.16	.02	.44	.05
Clover-alfalfa	Montana	.082	11.7	1.41	4.8	.58	.25	.03	.19	.02
Average of light honeys		.065	8.9	1.60	2.4	.41	.29	.05	.30	.06
Spanish needle	Illinois	.174	20.0	1.15	1.0	.06	.40	.02	.89	.05
Spanish needle	Illinois	.158	28.3	1.79	0.7	.04	.35	.02	.52	.03
Tulip poplar*	Georgia	.184	15.3	0.83	9.2	.50	1.04	.58	6.21	.38
Tulip poplar	Maryland	.521	9.3	0.17	..	..	..	..	1.48	.03
Mint	Florida	.143	5.4	0.37	..	..	..	..	1.14	.08
Buckwheat	Wisconsin	.129	14.1	1.09	33.5	2.59	0.70	.05	6.40	.49
Buckwheat	Wisconsin	.135	9.0	0.66	..	..	..	..	9.43	.71
Buckwheat	Wisconsin	.118	20.0	1.73	..	..	..	..	4.81	.41
Buckwheat*	Wisconsin	.074	10.3	1.37	8.9	1.12	.47	.06	0.46	.06
Buckwheat	New York	.095	8.2	0.85	3.1	0.33	.44	.05	9.53	1.00
Average of dark honeys		.173	14.0	1.00	9.4	.77	.56	.13	4.09	0.32
Honey-dew*	Wisconsin	.504	31.0	0.61	..	..	..	..	1.71	.03
Honey-dew*	Hawaii	.304	60.2	1.97	20.4	.67	.33	.01	0.85	.03
Average of honey-dew honeys		.404	45.6	1.29	..	..	..	..	1.28	.03

[9] American Public Health Association, "Standard Methods for the Examination of Water and Sewage," New York, 1925, 6th ed., p. 46.

[10] Kennedy, *J. Biol. Chem.*, **74,** 385 (1927).

[11] Elvehjem and Lindow, *J. Biol. Chem.*, **81,** 435 (1929).

[12] Spacu, *Bul. Soc. Stiinte Cluj.*, **1,** 284 (1922); *Chem. Abst.*, **17,** 1772 (1923); Biazzo, *Ann. chim. applicata*, **16,** 96 (1926); *Chem. Abst.*, **20,** 2029 (1926).

The range of sample weights used lay between 23 and 124 g. Their copper content was checked by means of a colorimeter against a reference solution containing 0.02 mg. of this element.

Determination of Manganese.—Manganese determinations were made by the periodate method of Willard and Greathouse[13] with certain modifications in procedure as suggested by Peterson and colleagues.[14,15] The method in question rests upon the comparison of color intensities of the permanganate ion. Aliquot portions of the several ash solutions, representing not less than 35 g. nor more than 228 g. of sample, were taken for comparison with a standard potassium permanganate solution, the volume of the latter being determined by the individual needs of the sample, but in every instance containing 0.05 mg. of manganese or a multiple thereof up to 0.2 mg.

Discussion

It is evident that the ash content and degree of pigmentation apparently bear some relationship to each other, for the dark honeys were found to contain more mineral matter than the light colored ones. Quantitative relationships with respect to these two major color differences cannot be set up, of course, because of the fact that honey is seldom derived exclusively from the nectar of one species of flower. But even with this limitation the general conclusion finds corroboration in the data of Browne[16] which, when subjected to a similar analysis, also reveal the fact that the light colored honeys which he examined contained less mineral matter than did the dark ones. This correlation of data cannot be extended beyond this point for analyses were not made to include manganese and copper since the clinical advantages of the presence of these elements in the diet were unknown at that time. A parallel is found, however, when more recent data, reported by foreign investigators, are reinterpreted. The data of Sundberg and Lundgren,[7] for example, although limited to seven samples, show the same trend in the silica, iron and manganese content of dark honeys in contrast to lesser pigmented ones. Similarly, this condition obtains in the iron and manganese data of Elser,[4] who examined honeys grown in Switzerland.

It is also significant that this preponderance of total mineral matter in the dark colored honeys is reflected both in the average and in the maximum quantities of the constituent elements thereof (Table II). The order of magnitude of the minima is also larger except for the silica content and probably, too, the iron, yet in the latter case comparisons appear hardly valid because of the unequal number of analyses in both groups.

It is indeed an interesting observation that buckwheat honey, which in the competition for consumer preference and price is often handicapped

[13] Willard and Greathouse, THIS JOURNAL, **39**, 2366 (1917).

[14] Lindow and Peterson, *J. Biol. Chem.*, **75**, 169 (1927).

[15] Skinner and Peterson, *ibid.*, **88**, 347 (1930).

[16] Browne, Bull. 110, Bur. Chem. U. S. Dept. Agric., 22–39 (1908).

TABLE II

VARIATION IN ASH, SILICA, IRON, COPPER AND MANGANESE CONTENT OF LIGHT AND DARK FLORAL HONEYS

	Floral Honey							
	Light				Dark			
Constituent	Samples	Min.	Max.	Av.	Samples	Min.	Max.	Av.
Ash[a]	10	0.04	0.16	0.06	10	0.07	0.52	0.17
Silica	10	7.20	11.70	8.90	10	5.40	28.30	14.00
Iron	10	1.20	4.80	2.40	6	0.70	33.50	9.40
Copper	10	0.14	0.70	0.29	6	.35	1.04	0.56
Manganese	10	.17	.44	.30	10	.52	9.53	4.09

[a] Per cent., other constituents in terms of mgs. per kg.

by its dark color and a not so delicate flavor, should contain, in comparison with clover and alfalfa honeys, strikingly more manganese and copper.

An explanation for the conditions which are noted above may conceivably be found in the suggestion that the characteristics and flavor of honey are influenced to a marked degree by nectar and pollen. They, in turn, may very well vary in composition and quality according as the plant which produced them is affected by such growth factors as the meteorological conditions prevailing in its habitat and the nature and fertility of the soil, as it possesses some peculiar ability to utilize nutrient materials or thrives because of some unique mineral requirements.

These studies on honey pigmentation will be continued in the hope of ascertaining whether or not any relationship exists between pollen and mineral content, particularly manganese. The observation of Famintzin and Przybytik[17] that the ash of the pollen of the pine, *Pinus sylvestris*, contains this element will be made the point of departure in extending this search to the pollens of those plant species which serve as sources of honey.

Summary

Data have been presented in support of the hypothesis that there apparently exists in honey a relationship between the degree of pigmentation and the quantity of mineral matter, notably manganese and copper, which it contains.

MADISON, WISCONSIN

[17] Famintzin and Przybytik, *J. Russ. Chem. Soc.*, 371 (1885); *J. Chem. Soc.*, **50**, 172 (1886).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CONSTITUTION OF STÄDELER'S TYROSINE SULFONIC ACID

BY FREDERICK R. CONKLIN[1] AND TREAT B. JOHNSON

RECEIVED FEBRUARY 24, 1932 PUBLISHED JULY 6, 1932

When proteins are nitrated, or halogenated, one definite point of attack in the molecule is the phenol nucleus of the aromatic amino acid tyrosine combined in the protein. Oswald[2] isolated from the hydrolysis products of several iodinated proteins the amino acid diiodotyrosine, which was shown to be identical with the iodine derivative obtained by direct iodination of tyrosine, and whose constitution was established by Wheeler and Johns.[3] Inouye's[4] observation that one of the hydrolytic products of nitrated silk fibroin is mono-nitrotyrosine was confirmed by the work of Johnson, who also established the constitution[5] of this tyrosine derivative.

Regarding the nature of the products of hydrolysis of sulfonated proteins we have very little knowledge outside of the data contributed by the early work of Mülder[6] and Loew.[7] The sulfonic acids resulting from treatment of proteins with sulfuric acid are usually obtained as amorphous substances with a varying content of sulfur, and it has been assumed that the change brought about by the action of this reagent involves a substitution in the aromatic nucleus of the amino acids, phenylalanine and tyrosine. No sulfonic acid derivative of either of these two amino acids has been identified, however, among the products formed by hydrolysis. In addition, while both of these amino acids have been shown to interact with sulfuric acid with formation of definite sulfonic acids,[8] the constitution of these respective substitution products has not been established with certainty.

We have now repeated the experiments of Städeler, who investigated the action of sulfuric acid on tyrosine in 1860, and have developed a practical method for preparing a definite mono-sulfonic derivative of this amino acid. It is easily obtained in excellent yield, and in a crystalline condition, and this acid obtained by our method is undoubtedly identical with the tyrosine-sulfonic acid originally described by Städeler. We did not obtain

[1] Cheney Brothers Graduate Scholar in Chemistry, 1930–1931.

[2] A. Oswald, *Z. physiol. Chem.*, **70,** 310 (1910); **71,** 200 (1911); **74,** 290 (1911); **75,** 353 (1911).

[3] Wheeler and Johns, *Am. Chem. J.*, **43,** 11 (1910).

[4] Inouye, *Z. physiol. Chem.*, **81,** 82 (1912).

[5] Johnson, THIS JOURNAL, **37,** 2598 (1915); see also Johnson and Kohmann, *ibid.*, **37,** 1863, 2164 (1915); Johnson, Hill and O'Hara, *ibid.*, **37,** 2170 (1915); and Johnson and Hill, *ibid.*, **38,** 1392 (1916).

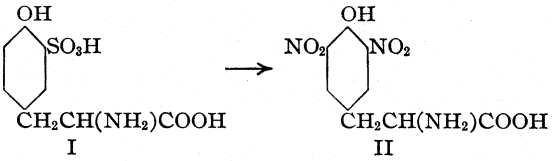
[6] Mülder, *Pogg. Ann.*, **37,** 594 (1836); *Chem. Zentr.*, 242 (1839).

[7] Loew, *J. prakt. Chem.*, [2] **3,** 180 (1871); [2] **5,** 433 (1872).

[8] Städeler, *Ann.*, **116,** 91 (1860); Erlenmeyer and Lipp, *ibid.*, **219,** 209 (1883).

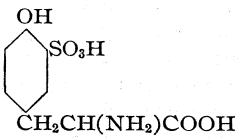
any evidence of the formation of a disulfonic acid derivative of tyrosine corresponding in structure to dinitrotyrosine or diiodotyrosine.

Of the two mono-sulfonic acid derivatives theoretically possible of formation by the action of sulfuric acid on tyrosine, namely, 2- and 3-sulfotyrosines, we now conclude that the acid described by Städeler is to be represented structurally by formula I. This was established by the fact that it interacts smoothly with nitric acid to form 3,5-dinitrotyrosine II with complete substitution of the sulfonic acid group by a nitro radical.



While it would be of interest to establish the presence of this acid I among the products of hydrolysis of a sulfonated protein, we have not made any serious attempts to accomplish such a separation. We are more especially interested at present in the possibility of utilizing tyrosine-3-sulfonic acid as the source of new types of pressor-bases, and for preparing other aromatic derivatives of immediate biochemical interest. The study of this compound is being continued.

Experimental Part

Preparation and Properties of Tyrosine-3-sulfonic Acid.[9]— 

Ten grams of pure crystallized tyrosine is thoroughly mixed with 32.5 g. (six mols) of cold concentrated sulfuric acid. The sulfonation starts immediately on adding tyrosine to the acid and the temperature of the mixture rises quickly to 55°. After the mixture is prepared, it is heated in an oil-bath at a temperature of 95–100° for one hour, and with constant stirring to insure uniformity of reaction. The acid solution is then cooled and poured into 800 cc. of cold water and the sulfuric acid removed quantitatively as barium sulfate by addition of barium hydroxide. After separation of the barium sulfate by filtration, the filtrate and washings are combined and finally concentrated under reduced pressure to a volume of about 70 cc. and this then allowed to stand in an ice chest. A portion of the tyrosine sulfonic acid will crystallize in the form of colorless fine needles. These were separated and the solution concentrated further to 30 cc. in volume and another crop of the pure sulfonic amino acid obtained. The total yield of the sulfonic acid obtainable by crystallization is about 90% of the theoretical. If crystallization is hurried by quick chilling of the solution the tyrosine sulfonic acid always separates in an amorphous condition. Tyrosine sulfonic acid exhibits the characteristic property of forming supersaturated solutions when dissolved in water and consequently the purification of the acid by crystallization is very slow.

Anal. Calcd. for $C_9H_{11}O_6NS$: N, 5.36; S, 12.25. Found: N, 5.33; S, 12.50.

Tyrosine-3-sulfonic acid shows no definite melting point but chars and decomposes

[9] The authors are indebted to the Cheney Brothers, Silk Manufacturers of South Manchester, Connecticut, for the supply of silk fibroin which was used in our research for the preparation of tyrosine.

rapidly when heated above 280°. It is insoluble in cold water, gives an opaque solution when digested with a large volume of boiling water, and also dissolves in warm methyl alcohol. The acid separates from methyl alcohol in an amorphous form when the solvent is evaporated, and it also separates from its aqueous solution in a similar form if the crystallization is hurried. The acid gives a deep violet coloration with ferric chloride solution, and also reacts with Millon's reagent to give a characteristic pink color. The barium, sodium and potassium salts are all amorphous substances which are very soluble in water. Attempts to bring about a reaction with potassium cyanate and phenyl isocyanate were unsuccessful. In other words, the characteristic reactivity of the tyrosine molecule is completely changed by introduction of the sulfonic acid group. The basicity of the α-amino radical is masked by the presence in the molecule of the three negative groupings—OH, SO_3H and COOH.

The Formation of 3,5-Dinitrotyrosine II from Tyrosine-3-sulfonic Acid.—Twenty-two grams of concentrated sulfuric acid is mixed with 3 g. of concentrated nitric acid and the liquid cooled to 5°. Three grams of tyrosine-3-sulfonic acid is then added to this mixed acid in small portions with constant shaking over a period of twenty minutes. The sulfonic acid dissolves completely, giving a light orange-colored solution and the temperature rises to about 25°. After completion of the nitration the acid mixture is poured into 800 cc. of cold water and the sulfuric acid quantitatively removed as barium sulfate. The resulting solution is then made strongly alkaline by addition of ammonia and concentrated to a volume of about 10 cc. under reduced pressure. A brick-red crystalline precipitate of an ammonium salt is obtained which is decomposed by washing with dilute hydrochloric acid. This treatment gave a crystalline substance which was identified as the hydrochloride of 3,5-dinitrotyrosine. It crystallized from hot water in beautiful yellow plates melting with effervescence at 230°. It did not respond to a test for sulfur. The yield of purified acid was about 1.0 g. The identity of this compound was established by comparison with a sample of the hydrochloride of 3,5-dinitrotyrosine prepared by Johnson and Kohmann[5] in 1915. There was no change in melting point when a mixture of the two salts was heated in a capillary tube. It is of interest to note here the stability of this nitration product of tyrosine. The 3,5-dinitrotyrosine hydrochloride prepared by Johnson and Kohmann actually showed no change in melting point after storage in the laboratory for sixteen years.

Anal. Calcd. for $C_9H_9O_7N_3 \cdot HCl$: N, 13.60; Cl, 11.54. Found: N, 13.55; Cl, 11.60.

This formation of dinitrotyrosine is another outstanding example of the easy replacement during nitration of a sulfonic acid group by the nitro radical. This interchange of sulfonic and nitro groups has been observed previously by several investigators.[10]

While tyrosine-3-sulfonic acid interacts smoothly with nitric acid with replacement of the sulfonic radical by a nitro group, an attempt to bring about a corresponding conversion into 3,5-dibromotyrosine[11] by the action of bromine was unsuccessful. This technique of establishing structure of aromatic compounds has been applied with success in other cases by several workers.[12]

[10] Neville and Winther, *Ber.*, **13**, 1946 (1880); Sakellarios, *ibid.*, **55**, 2846 (1922); Schmidt and Glutz, *ibid.*, **2**, 52 (1869); Armstrong, *Z. Chem.*, **14**, 517, 677 (1871); Zincke, *Ann.*, **339**, 202 (1905); Michler and Walden, *Ber.*, **14**, 2176 (1881); Datta and Varma, **41**, 2039 (1919).

[11] Von Gomp and Besanez, *Ann.*, **125**, 281 (1863); Mörner, *Z. physiol. Chem.*, **88**, 124 (1913).

[12] Datta and Bhoumik, THIS JOURNAL, **43**, 303 (1921); Sakellarios, *Ber.*, **55**, 2845 (1922); Sudborough, *J. Chem. Soc.*, **111**, 41 (1910); Elgersma, *Rec. trav. chim.*, **48**, 759 (1929); Suter, THIS JOURNAL, **53**, 1112 (1931).

An attempt was also made to establish the constitution of tyrosine-3-sulfonic acid by conversion into a cinnamic acid derivative through deaminization by digestion with methyl iodide and potassium hydroxide. This transformation is not accomplished without complete degradation of the greater part of the sulfonic acid. We did succeed in obtaining a small quantity of the desired cinnamic acid derivative, $HO_3S(OH)C_6H_3CH=CHCOOH$ in the form of its potassium salt, but the quantity formed was so small that this method of operating proved of no practical utility. This potassium salt was purified by crystallization from water. It reacted with concentrated sulfuric acid to give a red colored solution, but did not give color reactions when treated with ferric chloride solution or Millon's reagent. It had no definite melting point.

Anal. Calcd. for $C_{10}H_9O_6SK$: S, 10.80. Found: S, 10.66, 10.9.

Summary

1. When tyrosine is allowed to react with sulfuric acid at 95–100° it is converted smoothly into tyrosine-3-sulfonic acid.

2. The structure of this acid is established by the fact that it is converted into 3,5-dinitrotyrosine by the action of nitric acid.

NEW HAVEN, CONNECTICUT

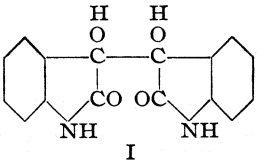
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF THE OZARKS]

SOME OBSERVATIONS CONCERNING THE STRUCTURE OF ISATIDE

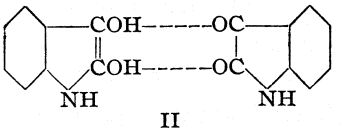
BY WARD C. SUMPTER

RECEIVED FEBRUARY 29, 1932 PUBLISHED JULY 6, 1932

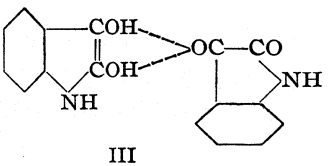
The isatin pinacol formula for isatide, I, proposed by Kohn[1] and by Lefèvre,[2] has been disputed by Heller.[3] Heller regards isatide as being a quinhydrone type of compound, II or III.



I



II



III

Isatide is best prepared by condensing isatin with dioxindole in alcoholic solution in the presence of piperidine. The condensation of a substituted dioxindole with isatin and of a substituted isatin with dioxindole should give rise to two different isatides if the quinhydrone formulation is correct.

[1] Kohn, *Ber.*, **49**, 2514 (1916); Kohn and Klein, *Monatsh.*, **33**, 929 (1912); Kohn and Ostersetzer, *ibid.*, **37**, 25 (1916).

[2] Lefèvre, *Bull. soc. chim.*, **19**, 113 (1916).

[3] Heller, *Ber.*, **49**, 1406 (1916); Heller and Lauth, *ibid.*, **62**, 343 (1929).

Wahl and Faivret[4] obtained a 5-methylisatide by condensing dioxindole with 5-methylisatin. The condensation of 5-methyldioxindole with isatin gives the same 5-methylisatide. This fact precludes acceptance of the quinhydrone formulation and strongly supports the symmetrical isatin pinacol formula.

Experimental

5-Methylisatide. A. From 5-methylisatin and dioxindole, Method of Wahl and Faivret.—Ten drops of piperidine was added to a solution of 1.9 g. of dioxindole and 2 g. of 5-methylisatin in 50 cc. of 95% ethyl alcohol and the whole heated on the water-bath under a reflux condenser for one hour. After cooling the precipitate was filtered off and washed repeatedly with small portions of alcohol. The straw colored powder so obtained could not be crystallized from any of the usual organic solvents. The yield was 3.1 g. or 81% of the theoretical. The substance softened at about 220° and melted with decomposition at 228–230°. Wahl and Faivret reported 229–230°.

B. From Isatin and 5-Methyldioxindole.—The procedure was identical with that described above. The substance softened at about 220° and melted with decomposition at 227–230°. A mixture of this substance with the 5-methylisatide prepared from dioxindole and 5-methylisatin melted with decomposition at 227–230°. The yield was 3 g. or 79% of the theoretical.

The writer is indebted to the Dow Chemical Co. for the gift of a generous supply of indigo from which the isatin and dioxindole used in this work were prepared.

Summary

The condensation of 5-methyldioxindole with isatin yields the same 5-methylisatide obtained by Wahl and Faivret from 5-methylisatin and dioxindole. In the light of this fact the unsymmetrical quinhydrone formulation for isatide is untenable. The isatin pinacol formula is probably correct.

[4] Wahl and Faivret, *Ann. chim.*, **5**, 314 (1926).

CLARKSVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE NUMBER OF STRUCTURAL ISOMERS OF CERTAIN HOMOLOGS OF METHANE AND METHANOL

BY DOUGLASS PERRY

RECEIVED MARCH 4, 1932 PUBLISHED JULY 6, 1932

A very ingenious general method for determining the number of structurally isomeric paraffin hydrocarbons has been published recently.[1] The purpose of this article is to extend the results previously given by applying this method to the computation of the number of structural isomers of hydrocarbons of the methane series of carbon contents ranging from twenty to forty, inclusive, and of hexacontane.

In order to calculate the number of structural isomers of a given paraffin hydrocarbon by the method referred to above, it is first necessary to know

[1] Henze and Blair, THIS JOURNAL, **53**, 3077 (1931).

the numbers of all structurally isomeric alcohols of the methanol series of carbon content not exceeding one-half that of the hydrocarbon. Table I represents the number of structurally isomeric saturated monohydric alcohols containing from twenty to thirty carbon atoms per molecule, computed according to the method of Henze and Blair,[2] and augments the values listed by them.

TABLE I

THE NUMBER OF STRUCTURALLY ISOMERIC HOMOLOGS OF METHANOL

Carbon content	Primary	Secondary	Tertiary	Total
21	5,622,109	5,806,256	3,287,448	14,715,813
22	14,715,813	15,256,265	8,677,074	38,649,152
23	38,649,152	40,210,657	22,962,118	101,821,927
24	101,821,927	106,273,050	60,915,508	269,010,485
25	269,010,485	281,593,237	161,962,845	712,566,567
26	712,566,567	747,890,675	431,536,102	1,891,993,344
27	1,891,993,344	1,990,689,459	1,152,022,025	5,034,704,828
28	5,034,704,828	5,309,397,294	3,081,015,684	13,425,117,806
29	13,425,117,806	14,187,485,959	8,253,947,104	35,866,550,869
30	35,866,550,869	37,977,600,390	22,147,214,029	95,991,365,288

The inverse ratios of consecutive numbers in the last column are very nearly constant, but always slightly increasing, and possess ever diminishing first differences. Assuming that the numbers in the last column are in geometric progression, and extrapolating the value of the average common ratio over the carbon content interval from 30 to 35, the number of structurally isomeric alcohols of the formula $C_{35}H_{71}OH$ can be estimated as: $T_{35} = (2.688)^5 T_{30} = 1.35 \times 10^{13}$. Taking the average common ratio over the carbon content interval from 30 to 40 as 2.695, by a similar computation the corresponding value for $C_{40}H_{81}OH$ is 1.94×10^{15}.

Table II contains the number of structurally isomeric hydrocarbons of the methane series, and supplements the results previously found.[3] The

TABLE II

THE NUMBER OF STRUCTURALLY ISOMERIC PARAFFINS

Carbon content	Number of isomers	Carbon content	Number of isomers
19	148,284	31	10,660,307,791
21	910,726	32	27,711,252,769
22	2,278,658	33	72,214,088,660
23	5,731,580	34	188,626,236,139
24	14,490,245	35	493,782,952,902
26	93,839,412	36	1,295,297,588,128
27	240,215,803	37	3,404,490,780,161
28	617,105,614	38	8,964,747,474,595
29	1,590,372,121	39	23,647,478,933,969
		60	22,158,734,535,770,411,074,184

[2] Henze and Blair, THIS JOURNAL, **53**, 3042 (1931).

[3] Ref. 2, p. 3084.

number of isomers of $C_{19}H_{40}$ was found to be in error, and the correct value is here given. As in the case of the alcohols, the numbers of structurally isomeric hydrocarbons also form an approximate geometric progression. Here again the inverse ratios of successive numbers are always slightly increasing, and have decreasing first differences. The extrapolated average inverse ratio of consecutive numbers over the carbon content interval from 60 to 70 is 2.72, and hence the value for $C_{70}H_{142}$ is approximately 4.91×10^{26}.

Several corrections are to be noted in the original papers by Henze and Blair. On line 2, p. 3045, for "$(n-1)6$ an integer," read $(n-1)/6$ an integer. In the discussion of the number of hydrocarbons of even carbon content of group A, p. 3080, line 19, the factor $^1/_2$ should be inserted to make the formula read correctly. This remark also applies to the formula for hydrocarbons of odd carbon content resulting from joining alkyls of $(N+1)/2$ and $(N-1)/2$ carbon atoms through an intermediate carbon atom, p. 3080, line 36. In group B, type b, Case 2, page 3082, line 23, it might be well to mention explicitly that j and k cannot interchange values, which may be expressed by requiring that j always exceed k. For completeness, it may be added that in the formula for compounds of odd carbon content of Group A, it is implied that the definition of T_0 is unity. These corrections apply to the references noted, but were correctly applied in the computations of the authors.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BAKELITE CORPORATION]

MOLECULAR REARRANGEMENT IN THE HYDROLYSIS OF CHLOROTOLUENES WITH ALKALI

BY V. E. MEHARG AND IVEY ALLEN, JR.

RECEIVED MARCH 8, 1932 PUBLISHED JULY 6, 1932

It is known that molecular rearrangement takes place when ortho or para chlorobenzene sulfonic acid is fused with potash, both compounds yielding resorcinol by this treatment.[1] It now appears that such a rearrangement may be general with halogen substituted benzenes carrying aliphatic side chains. We have carried out a number of experiments on the hydrolysis of substituted chlorobenzenes carrying normal aliphatic side chains and have been singularly unsuccessful in obtaining pure products. This was particularly apparent in the case of the products obtained from the hydrolysis of ortho and para chloro substituted derivatives of ethylbenzene, normal butylbenzene, and normal amylbenzene. These compounds are not adequately described in the literature and the phenols derived from them have been described[2] but there are no quantitative methods for purifying

[1] Beilstein, 4th ed., Vol. VI, p. 796.

[2] Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

them in the presence of their isomers. The para substituted phenols in general have higher melting points than the corresponding ortho and meta derivatives but usually are very close to the meta derivatives in boiling point and many other properties. The fact that in some cases where we expected to obtain the para compounds the product, when purified by careful fractional distillation, distilled at almost exactly the correct point and yet failed to crystallize on cooling led us to believe that the meta isomer might be present as an impurity. A comparison of the properties of the product derived from *p*-ethylchlorobenzene with a sample of *p*-ethylphenol from another source seemed to confirm this explanation.

As a final check on the above we have carried out the hydrolysis of *o*- and *p*-chlorotoluenes in sodium hydroxide at temperatures above 300° and found *m*-cresol to be present in the product from each. The hydrolyses were carried out in a manner similar to that used by Meyer and Bergius[3] for the hydrolysis of chlorobenzene. These authors state that *p*-cresol is easily obtained from chlorotoluene, but do not state which chlorotoluene. In our experiments the purified phenolic portion from the *o*-chlorotoluene showed a *m*-cresol content of 25.3% and that from the para 38.2%. There was some slight evidence that all three cresols were present in each case but our method of analysis was not sufficiently accurate to detect small amounts of ortho and para. A slightly modified Raschig nitration method[4] was used for the meta determinations. This has been checked thoroughly in this and other laboratories and can be relied upon with certainty to give results accurate to 2% of the true value under our conditions.

Experimental

Hydrolysis of Chlorotoluenes.—The autoclave was 61 cm. long by 7 cm. inside diameter, and was fitted with a thermocouple well and flexible connections to a pressure gage and relief valve. It was made of carbon steel and the capacity was about 2.2 liters. It was heated electrically and was mounted on a shaking machine. The *o*- and *p*-chlorotoluenes used were obtained from the Eastman Kodak Company and were not given any further purification before use. The para compound had a freezing point of 7.1°. The melting point is given in the literature as 6.5–7.5°.

One hundred twenty-six grams (one mole) of *o*-chlorotoluene, 1332 g. (5 moles) of 15% sodium hydroxide, and 10 g. of freshly reduced copper powder were heated together for two hours at 315–320°. The shaking machine was run intermittently (five minutes on, ten minutes off). About two hours was required to raise the reaction mixture to the required temperature and a somewhat longer time for it to cool. When cold the contents were removed from the autoclave and extracted with ether. The water layer was then acidified and again extracted. The yield of crude alkali-soluble material was 60 g. *p*-Chlorotoluene treated in the same manner yielded 63 g. of crude product.

The greater part of the products from each of the runs described above was fractionated through a column of good efficiency built to handle small amounts of material. The data from the distillations and analyses were:

[3] Meyer and Bergius, *Ber.*, **47**, 3155 (1914).

[4] *Z. angew. Chem.*, **31**, 759 (1900).

	From *o*-chlorotoluene	From *p*-chlorotoluene
Still charge	32.9 g.	40.0 g.
Fraction 197–202°	9.7 g.	26.8 g.
Fraction 202–235°	0.4 g.	0.5 g.
Total distillate 182–235°	25.9 g.	30.2 g.
Meta cresol in 197–202° cut	67.5%	43.1%

When these results are calculated back to the total crude yields (parts of which were used for another purpose) we find that *o*-chlorotoluene yielded 55.4% of pure mixed phenols, calculated as cresol, and 25.3% of this material was *m*-cresol. The corresponding figures for *p*-chlorotoluene are 55.5 and 38.2%. No trace of phenol was found in either product.

Preparation and Hydrolysis of Ethylchlorobenzenes.—The products obtained from the chlorination of ethylbenzene were carefully fractionated and two fractions separated, one boiling chiefly at 180°, the other at 185°. Tohl and Eberhard[5] give the boiling point for *p*-ethylchlorobenzene as 180–182°. The fraction boiling at 180° yielded on oxidation with alkaline permanganate an acid which melted at 130–132°. *o*-Chlorobenzoic melts at 137°. The meta and para acids both melt much higher so the material boiling at 180° is *o*-ethylchlorobenzene. Both fractions were hydrolyzed in a manner similar to that used for the chlorotoluenes and the products purified in the same manner. Since the higher boiling fraction was not identified and might therefore contain some of the meta compound, its hydrolysis products will not be discussed at length. That which was obtained from several runs on the ortho was combined before purification and on distillation, cuts were taken as follows: 168–205°, 20.7 g.; 205–211° (205°), 45.5 g.; 211–218°, 7.8 g.; 218–222° (219°), 112.2 g.; 222–245°, 5.2 g. The total still charge was 224.5 g. Temperatures in parentheses are points at which the larger portions distilled. Boiling points given in the literature for ethylphenols are:[6] ortho, 206.5–207°; meta, 217°; and para, 218°. The lower boiling constituent is undoubtedly the ortho compound and the fraction boiling at 218–222° is probably a mixture of meta and para with meta largely in excess. It did not crystallize when seeded with crystalline *p*-ethylphenol from another source. The refractive index (n_D) was 1.5294 at 25°; *p*-ethyl gives 1.5288 for the supercooled liquid. A phenylurethan was prepared by the method of Fromm and Eckard[7] and it melted at 133–137°. The phenylurethan from *p*-ethylphenol melts at 120° and that from the meta at 138.8°.[8]

Summary

Ortho and para chlorotoluenes when hydrolyzed with sodium hydroxide undergo partial molecular rearrangement, yielding a mixture of products containing *m*-cresol.

Results on the hydrolysis of *o*-ethylchlorobenzene indicate that the rearrangement is general.

BLOOMFIELD, NEW JERSEY

[5] Beilstein, 4th ed., Vol. V, p. 354.

[6] Beilstein, 4th ed., Vol. VI, pp. 471–472.

[7] Eckard, *Ber.*, **56**, 948 (1923).

[8] Steinkopf and Höpner, *J. prakt. Chem.*, [2] **113**, 137 (1926).

[CONTRIBUTION FROM THE SCHOOL OF PHARMACY OF THE UNIVERSITY OF THE PHILIPPINES]

THE ALKALOIDS OF ARGEMONE MEXICANA

BY ALFREDO C. SANTOS AND PACIFICA ADKILEN

RECEIVED MARCH 10, 1932 PUBLISHED JULY 6, 1932

Many years ago Schlotterbeck[1] has shown that *Argemone mexicana*,[2] which is more familiarly known as mexican or prickly poppy, does not contain morphine. He isolated two alkaloids from this plant and on the basis of precipitation and color reactions he concluded that one of them was berberine. He identified the other alkaloid as protopine because of its melting point (204°) and color reactions.

Since then many alkaloids of the berberine type have been reported in the literature. According to Feist[3] palmatine gives also an acetone compound and responds to other reactions which Gordin[4] used for the identification of berberine. It appears, therefore, that the identification of berberine can no longer be done by precipitation and color reactions alone. In view of the foregoing reasons and of the fact that Schlotterbeck did not analyze his alkaloids, the present authors deemed it necessary to reinvestigate this plant.

By a method of isolation described in the experimental part, two alkaloids have been isolated from *Argemone mexicana*. One is a quaternary and the other is a tertiary base. The former was converted by reduction into a colorless tertiary base melting at 173–174° which by analysis and mixed melting point proved to be identical with tetrahydroberberine. The second base crystallized from a mixture of chloroform and methanol in nice monoclinic prisms melting at 207°. It responded to all the color reactions of protopine and on the basis of elementary analysis and mixed melting point with authentic material kindly furnished by E. Merck, Darmstadt, it was recognized as protopine.

Therefore, the assumption of Schlotterbeck that *Argemone mexicana* contains berberine and protopine proved to be correct.

Experimental

The material used consisted of whole plants collected at San Juan, La Union, and carefully deprived of the seeds; 568 g. of the air-dried powdered material was extracted until free from alkaloids with alcohol acidified with acetic acid. The alcohol was recovered from the alcoholic extract, the residue taken up with acidified water and filtered. The filtrate was first shaken out with ether in acid solution to remove neutral and indifferent substances, then rendered alkaline with potassium hydroxide and

[1] Schlotterbeck, THIS JOURNAL, **24**, 238 (1902).

[2] A native of tropical America. Introduced into the Philippines and known locally as *diluariu*, *kachumba* and *kasubang-aso*.

[3] Feist, *Arch. Pharm.*, **245**, 596 (1907).

[4] Gordin, *ibid.*, **240**, 146 (1902).

shaken out again with ether. The aqueous portion (A) was acidified with hydrochloric acid and set aside. On spontaneous evaporation of the ether a partly crystalline and sirupy residue remained. It was dissolved in diluted hydrochloric acid; rendered alkaline with potassium hydroxide and shaken out again with ether, this process being repeated many times until a white residue was left. This was dissolved in a little chloroform and an equal amount of methanol added. After three weeks' standing clusters of nice monoclinic prisms melting at 207°[5] separated. The melting point of a mixture of an equal amount of these crystals and protopine (m. p. 207°) furnished by E. Merck, Darmstadt, was 207°. The crystals gave the following color reactions: (1) with sulfuric acid, deep blue-violet; (2) with Froehde's reagent, violet-green changing to deep blue and finally becoming green; (3) with Mandelin's reagent, violet, then bluish-green, and finally blue; (4) with concentrated nitric acid, colorless in the cold, turning yellow on heating. The microanalysis gave values agreeing fairly with the values calculated for protopine.

Anal. Subs., 2.371 mg.: CO_2, 5.893 mg.; H_2O, 1.261 mg. Calcd. for $C_{20}H_{19}O_5N$: C, 67.95; H, 5.48. Found: C, 67.78; H, 5.95.

Tetrahydroberberine.—The yellow aqueous acid solution (A) that had been set aside in the isolation of protopine was reduced with zinc dust and sulfuric acid until the solution became almost colorless and filtered. The filtrate was cooled rapidly, treated with ammonia water until the precipitated zinc hydroxide redissolved and shaken out with ether. The ethereal solution was repeatedly shaken with dilute potassium hydroxide, washed with a little water and dried. On concentrating the ether crystals melting at 173–174°[6] separated. The melting point of a mixture of these crystals with tetrahydroberberine (m. p. 173–174°) was 173–174°.

Microanalysis. Subs., 2.720 mg.: CO_2, 7.089 mg.; H_2O, 1.509 mg. Subs., 2.609 mg.: AgI, 3.558 (Zeisel–Pregl–Friedrich). Calcd. for $C_{20}H_{21}O_4N$: C, 70.74; H, 6.24; OCH_3, 18.29. Found: C, 71.08; H, 6.21; OCH_3, 18.01.

Summary

The alkaloids of *Argemone mexicana* have been correctly identified as berberine and protopine.

MANILA, P. I.

[5] The melting point of pure protopine is reported at 207° by W. H. Perkin, Jr., *J. Chem. Soc.*, **109**, 1023 (1916), and by P. W. Danckwortt, *Arch. Pharm.*, **250**, 615 (1912).

[6] Späth and Polgar, *Monatsh.*, **52**, 117 (1929), reported that pure tetrahydroberberine melts at 173–174°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

THE REACTION BETWEEN DIETHYLAMINE AND ETHYLENE OXIDE

BY W. H. HORNE AND R. L. SHRINER

RECEIVED MARCH 10, 1932 PUBLISHED JULY 6, 1932

β-Diethylaminoethanol is an important intermediate in the preparation of alkylamino esters. The reaction between diethylamine and ethylene oxide should furnish a method of preparation which would be superior to the reduction of diethylaminoacetic ester[1] or the action of diethylamine on ethylene chlorohydrin[2] because of the greater ease in the isolation of the product. The starting materials are now available commercially and inexpensive. The purposes of the present investigation were (1) to determine the optimum conditions for the preparation of β-diethylaminoethanol and (2) to separate and identify some of the higher boiling compounds which are always formed in reactions involving ethylene oxide.

In 1863, just four years after he had first prepared ethylene oxide,[3] Wurtz noted its reaction with ammonia.[4] Since that time the action of ethylene oxide on ammonia,[5] primary, secondary and tertiary amines,[6] hydrazines,[7] amides and imides[8] has been investigated. Substituted ethylene oxides[8,9] have also been shown to react with ammonia and amines to yield various amino alcohols. These investigations were carried out before ethylene oxide was readily available, so no complete study of the combination of diethylamine and ethylene oxide has been published. Quite different experimental conditions were used by the previous investigators and no general procedures were described.

It was found that pure dry diethylamine did not react with ethylene oxide but in the presence of water or alcohol the reaction would take place. A study was made of the effect of various solvents and the data obtained are summarized in Table I of the Experimental Part. It is evident that methyl and ethyl alcohols afford a smooth, rapid absorption of ethylene

[1] Gault, *Compt. rend.*, **145**, 126 (1907); Bouveault and Blanc, *Bull. soc. chim.*, **31**, 1210 (1904).

[2] Ladenburg, *Ber.*, **14**, 1878 (1881).

[3] Wurtz, *Ann. chim. phys.*, **55**, 427 (1859).

[4] Wurtz, *ibid.*, **69**, 381 (1863).

[5] (a) Knoor, *Bull. soc. chim.*, **22**, 499 (1899); (b) Henry, *ibid.*, **25**, 978 (1901); (c) Krassuskii, *Compt. rend.*, **146**, 236 (1908).

[6] (a) Demole, *Ann.*, **173**, 127 (1874); (b) Knoor and Matthes, *Bull. soc. chim.*, **28**, 592 (1902); (c) Knoor and Brownsdon, *ibid.*, **30**, 921 (1903); (d) Gabel, *ibid.*, **38**, 600 (1925); (e) Roithner, *Monatsh.*, **15**, 655 (1894).

[7] Barnett, *Proc. Chem. Soc.*, **28**, 259 (1912); Ref. 6e.

[8] Gabriel, *Ber.*, **50**, 819 (1917).

[9] Krassuskii, *Compt. rend.*, **146**, 236 (1908); *Bull. soc. chim.*, **42**, 1151 (1927); *J. chim. Ukraine*, **1**, 65, 68, 398 (1925); *Chem. Abs.*, **20**, 2820 (1926).

oxide resulting in a good yield of β-diethylaminoethanol. Methyl alcohol was easier to separate by fractional distillation and hence is the best solvent. There was no evidence that the ethylene oxide reacted with the solvent under the conditions used.

A series of experiments was carried out to determine the best temperature for the reaction. If diethylamine containing a little water and liquid ethylene oxide are mixed at room temperature in a closed vessel the combination takes place slowly at first, but as the mixture warms up it finally proceeds with explosive violence.[10] It seems probable that an addition compound is first formed similar to that between Grignard reagents and ethylene oxide[11] which must be subsequently rearranged. It was found that a temperature range of 45–60° permitted a smooth, rapid absorption of gaseous ethylene oxide. Below 45° the absorption was slow and above 60° the reaction also slowed down due to the diminished solubility of the ethylene oxide in the amine. By carrying out the reaction at 45–60° the addition compound is rearranged as fast as it is formed, thus avoiding a violent reaction. It is interesting to note that this temperature range is the same as that used to rearrange the Grignard addition compounds.

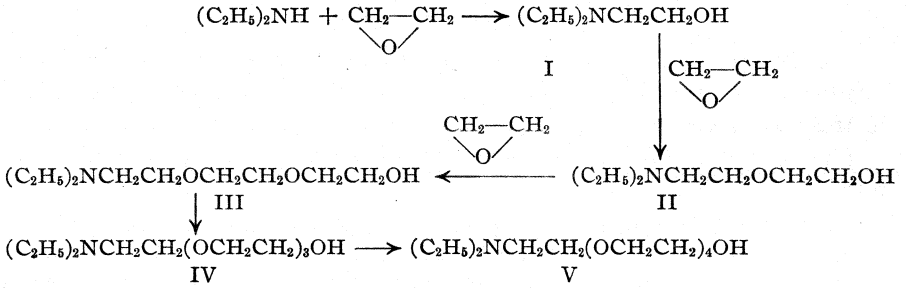
The results of variations in the mole ratio of reactants are also given in Table I. It is evident that the best yield was obtained with a ratio of about 1.3 moles of ethylene oxide to one mole of diethylamine (Run 9). The very slightly higher yield in Run 10 does not justify the use of the additional half mole of ethylene oxide. From Table II it will be noted that as the amount of ethylene oxide was increased the amount of unreacted diethylamine decreased but the percentage of material boiling above β-diethylaminoethanol was increased. These high boiling fractions from several runs were combined and carefully fractionated and two of the fractions definitely identified as the mono-β-diethylaminoethyl ether of ethylene glycol (II) and mono-β-diethylaminoethyl ether of diethylene glycol (III). Analyses and molecular refractivities of the two highest boiling fractions indicated that they are the mono-β-diethylaminoethyl ethers of triethylene glycol (IV) and tetraethylene glycol (V), respectively. These compounds represent the progressive addition of ethylene oxide and are of considerable theoretical interest, since they constitute further examples of bifunctional reactions discussed by Carothers in connection with chain polymerization.[12] They are evidently formed according to the reactions shown.

Compounds II, III, IV and V represent very low molecular weight chain molecules with different functional groups on the ends of the chain. Cyclic

[10] Staudinger [*Ber.*, **62**, 2395 (1929)] has also recorded the explosive polymerization of ethylene oxide.

[11] "Organic Syntheses," J. Wiley and Sons, Inc., New York, Vol. VI, 1926, p. 56.

[12] Carothers, *Chem. Rev.*, **8**, 353 (1931).



polymerization was blocked by the tertiary amino group. The presence of the alcohol group was demonstrated by reaction with *p*-nitrophenyl isocyanate[13] or with *p*-nitrobenzoyl chloride. The amino group was indicated by the formation of a salt with hydrochloric acid. In the transformation of I ⟶ II ⟶ III the addition of the ethylene oxide can take place at only one end of the chain instead of both ends as in the linear polymers of ethylene oxide alone. That compound II was actually formed from I was shown by treating pure β-diethylaminoethanol in methyl alcohol solution with ethylene oxide and isolating the compounds II and III. Similarly III can be obtained from II, IV from III and V from IV.

TABLE I

EFFECT OF SOLVENTS

Run	Solvent, g.	Diethylamine, g. *A*	Ethylene oxide, g. *B*	Mole ratio *B*/*A*	Yield Grams	Yield %	Time, hours
1	None	60.0	0.5	0.0138	..	0.00	6
2	H_2O 2.5	54.5	21	.639	39	45.0	10
3	H_2O 2.5	49.0	30	1.02	38	48.4	15
4	C_6H_6 50, H_2O 5	40.0	18	0.747	30	46.8	4
5	C_6H_6 100, H_2O 5	58.5	94	2.67	40	42.7	15
6	C_2H_5OH (95%) 40	40	26	1.08	43	67.1	1.5
7	C_2H_5OH (95%) 40	40	44	1.83	48	74.9	4
8	CH_3OH 40	40	28	1.16	40.5	63.2	1.33
9	CH_3OH (absolute), 40	40	32	1.33	48	74.9	2
10	CH_3OH 40	40	43	1.78	49	76.5	2.5

TABLE II

EFFECT OF INCREASING AMOUNTS OF ETHYLENE OXIDE ON COMPOSITION OF THE REACTION MIXTURE

Run	Ethylene oxide added, g.	Diethylamine recovered, g.	β-Diethylaminoethanol, g.	Higher fraction 80–135°, 7–10 mm., g.	Residue, above 135°, g.
1	18	7.64	34	5	1.0
2	26	7.15	43	7.5	2.5
3	28	6.7	40.5	7.0	1.5
4	32	6.17	48	10.0	2.0
5	43	3.87	49	17.5	4.0

[13] Horne and Shriner, THIS JOURNAL, **53**, 3186 (1931); Shriner and Cox, *ibid.*, **53**, 1601 (1931).

Experimental Part

The results of the experiments carried out to determine the optimum conditions for the preparation of β-diethylaminoethanol are summarized in the two tables.

The best procedure for the production of β-diethylaminoethanol (Run 9) was the following.

β-Diethylaminoethanol.—Forty grams of diethylamine was dissolved in 40 g. of methyl alcohol as solvent. The mixture was warmed to 45–60° and a fairly rapid stream of ethylene oxide passed through the reaction mixture. The flow of ethylene oxide was adjusted to keep the heat of the reaction from raising the temperature of the mixture above 60°. The maximum rate of addition was achieved in this manner. After two hours, 32 g. (8 g. excess) of ethylene oxide had been added. By fractional distillation *in vacuo* 48 g. of β-diethylaminoethanol (74.9% of the theoretical) was obtained. The residues in the flask (about 15 g.) from several runs were combined and fractionated as described below.

The product of the reaction was identified as β-diethylaminoethanol by means of its chemical and physical properties. It was found to contain hydrogen replaceable by metallic sodium, and to produce a distinctly alkaline aqueous solution. It was soluble in water, ether, benzene, petroleum ether and acetone. Its hydrochloride salt was precipitated from ether solution. This salt is very hygroscopic. Physical Properties: colorless, hygroscopic liquid, which turns yellow on standing; b. p. 163° at 760 mm. and 42–44° at 8 mm.; n_D^{25} 1.4400; d_{25}^{25} 0.8601; M_D calcd., 35.02; found, 35.81.

Anal. Calcd. for $C_6H_{15}ON$: N, 11.95. Found: N, 11.40.

To establish further the identity of the compound the *p*-nitrophenyl urethan was prepared by mixing β-diethylaminoethanol with *p*-nitrophenyl isocyanate in benzene solution. Evaporation of the benzene left the urethan, which was recrystallized from carbon tetrachloride as yellow crystals, m. p. 59–60° (corr.).

Anal. Calcd. for $C_{13}H_{19}O_4N_3$: N, 14.95. Found: N, 14.66.

The hydrochloride salt of this urethan was obtained by dissolving the urethan in dry acetone and precipitating as yellow crystals with dry hydrogen chloride. This derivative was recrystallized from 95% alcohol as fine yellow crystals, decomp. 200–210°.

Anal. Calcd. for $C_{13}H_{20}O_4N_3Cl$: Cl, 11.17. Found: Cl, 11.12.

Fractionation of the High Boiling Residues.—The residues from the distillation of ten runs from the preparation of β-diethylaminoethanol were combined and fractionally distilled *in vacuo* with the following results.

Fraction	Temp. at 7 mm., °C.	Vol. (approx.), cc.
1	80– 90	4
2	90– 95	15
3	95–100	25
4	100–120	15
5	120–130	30
6 (Residue)	Above 130	10
	Total	99

Fractions 2 and 3 were combined and redistilled, yielding about 27 cc. of material boiling between 92 and 95° (Fraction A). Fraction 5 was redistilled and about 22 cc. of material was obtained between 123 and 128° (Fraction B). In this way these two

fractions represented the two chief components of the mixture. The residue was a dark brown viscous material from which no definite product could be isolated.

Identification of Fraction A as the Mono-(β-diethylaminoethyl) Ether of Ethylene Glycol.—Fraction A was a colorless hygroscopic liquid with an odor similar to that of β-diethylaminoethanol. It reacted with sodium and was soluble in water, benzene, alcohol, ether and acetone. The aqueous solution was alkaline. Its hydrochloride was precipitated from ether by dry hydrogen chloride and found to be very hygroscopic. Physical properties: b. p. 92–95° at 7 mm.; n_D^{25} 1.4457; d_{25}^{25} 0.9399; M_D, calcd., 44.52; found, 45.65.

Anal. Calcd. for $C_8H_{19}O_2N$: N, 8.70. Found: N, 8.77.

To further establish the identity of this compound the *p*-nitrophenyl urethan hydrochloride was obtained by treating fraction A with *p*-nitrophenyl isocyanate in benzene solution. Addition of dry hydrogen chloride gave an orange oil which was crystallized from 95% alcohol and washed with acetone; light yellow crystals, m. p. 152–153° (corr.).

Anal. Calcd. for $C_{15}H_{24}O_5N_3Cl$. Cl, 9.81. Found: Cl, 9.77.

Identification of Fraction B as the Mono-(β-diethylaminoethyl) Ether of Diethylene Glycol.—Fraction B was also a light yellow, hygroscopic, viscous liquid. It reacted with metallic sodium, and produced a distinctly alkaline aqueous solution. It was soluble in water, ether, acetone and benzene. Its hydrochloride salt was precipitated from ether and found to be hygroscopic. Physical properties: b. p. 123–128° at 7 mm.; n_D^{25} 1.4534; d_{25}^{25} 0.9763; M_D, calcd., 55.00; found, 56.80.

Anal. Calcd. for $C_{10}H_{23}O_3N$: N, 6.83. Found: N, 6.71.

The *p*-nitrobenzoate was obtained by treatment with *p*-nitrobenzoyl chloride. The product was obtained as light yellow crystals from 95% alcohol; m. p. 121.5–122° (corr.).

Anal. Calcd. for $C_{17}H_{26}O_6N_2$: N, 7.91. Found: N, 8.09.

Attempts to prepare derivatives of fractions A and B with the following reagents failed: with α-naphthyl isocyanate and methyl-*p*-toluenesulfonate, viscous, non-crystallizing products were obtained; with chloroplatinic acid and picric acid no insoluble products were produced.

Conversion of β-Diethylaminoethanol into Mono-(β-diethylaminoethyl) Ether of Ethylene Glycol.—Twelve grams of β-diethylaminoethanol was dissolved in 10 g. of methyl alcohol and ethylene oxide passed into the solution which was kept at 50°. In thirty minutes 14 g. of ethylene oxide was absorbed. The solvent was distilled and the residual oil fractionated. About 7 g. of unreacted β-diethylaminoethanol was recovered and 4 g. of material boiling 92–95° at 7 mm. was obtained. This last fraction agreed in its properties with the mono-(β-diethylaminoethyl) ether of ethylene glycol.

Separation of Fraction 6.—After a considerable number of the residues constituting fraction 6 above had been obtained, they were combined and carefully fractionated *in vacuo* using a column packed with carborundum. After repeated distillation two fractions were obtained; C, boiling between 164–172° at 7 mm.; and D, boiling 190–200° at 7 mm.

Identification of Fraction C as the Mono-(β-diethylaminoethyl) Ether of Triethylene Glycol.—Fraction C was a yellow, very viscous hygroscopic liquid. It was soluble in water, ether, alcohol and acetone but was less soluble in benzene than fraction B. Physical properties: b. p. 164–172 at 7 mm., n_D^{25} 1.4570, d_{25}^{25} 1.0237, M_D calcd. 65.48, found 66.31.

Anal. Calcd. for $C_{12}H_{27}O_4N$: N, 5.61. Found: N, 5.65.

Identification of Fraction D as the Mono-(β-diethylaminoethyl) Ether of Tetraethylene Glycol.—Fraction D was a dark yellow viscous hygroscopic liquid.

It was soluble in water, ether, alcohol, acetone but slightly soluble in benzene and insoluble in petroleum ether. Physical properties: b. p. 190–200° at 7 mm., n_D^{25} 1.4622, d_{25}^{25} 1.0510, M_D calcd. 75.96, found, 74.92.

Anal. Calcd. for $C_{14}H_{31}O_5N$: N, 4.77. Found: N, 4.72.

No solid derivatives of Fractions C and D could be obtained.

Summary

1. β-Diethylaminoethanol may be prepared conveniently by the combination of diethylamine with ethylene oxide in methyl alcohol solution at a temperature range of 45–60°.

2. The above reaction also produces chain molecules corresponding to the addition of two, three, four and five molecules of ethylene oxide to one of diethylamine. The mono-(β-diethylaminoethyl) ethers of ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol have been isolated and characterized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND STATION OF THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE TOXICITY TO GOLDFISH OF CERTAIN ORGANIC THIOCYANATES AND ISOTHIOCYANATES[1]

BY NATHAN L. DRAKE AND RUTH L. BUSBEY

RECEIVED MARCH 10, 1932 PUBLISHED JULY 6, 1932

There appear in the literature several scattered references to investigations concerned with the possible value of thiocyanates and isothiocyanates as insecticides.

Moore[2] reported that, molecule for molecule, allyl isothiocyanate is more toxic against house flies (*Musca domestica* L.) than chloropicrin. Later, allyl isothiocyanate was found by Tattersfield and Roberts[3] to be the most toxic to wireworms (*Agriotes*) of all compounds tested by them. Probably two or more species were used in the tests. More recently, Neifert and co-workers[4] in tests with fumigants against the rice weevil (*Calendra oryzae* L.) and the flour beetle (*Tribolium confusum* Duv.) and the granary weevil (*Calendra granaria* L.) found that methyl and ethyl thiocyanates, and allyl isothiocyanates were more effective than carbon bisulfide.

In another investigation of possible fumigants, Roark and Cotton[5] found

[1] From a thesis submitted by Ruth Lawless to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Master of Science.

[2] Moore, *J. Agr. Research*, **10**, 365–71 (1917).

[3] Tattersfield and Roberts, *J. Agr. Sci.*, **10**, 119–232 (1920).

[4] Ira E. Neifert and co-workers, "Fumigation against Grain Weevils with Various Volatile Organic Compounds," U. S. D. A. Dept. Bull. 1313 (1925).

[5] Roark and Cotton, "Tests of Various Aliphatic Compounds as Fumigants," Tech. Bull. 162 of the U. S. Dept. of Agriculture, March, 1930.

ethyl thiocyanate and ethyl and allyl isothiocyanates very effective against the rice weevil (*Calendra oryzae* L.); in fact, these substances were shown to be about as effective as the now widely used ethylene oxide.

A number of patents covering insecticides and fungicides which contain as the active constituent aliphatic or aromatic thiocyanates have been issued.[6] Most of the compounds mentioned in these patents are aromatic thiocyanates, or aromatic hydrocarbons with the thiocyanate group substituted for hydrogen in an alkyl side chain. Only the last two references mention specifically pure aliphatic thiocyanates. None of the patents relate to isothiocyanates.

The present paper is the report of a study, according to the method of Gersdorff,[7] of the toxicity to goldfish of a number of other thiocyanates and isothiocyanates. It has been found that compounds and plant extractives highly toxic to fish are more likely to have value as insecticides than materials which are non-toxic to fish. This study has been made in the hope of finding additional thio- and isothiocyanates which may prove to be valuable insecticides.

Preparation of Materials

n-Amyl and isoamyl isothiocyanates were prepared from the corresponding amines by the method of Slotta and Dressler.[8] The boiling points of the products used in the toxicity tests were 193.5–196.5°, and 190–192°, respectively (uncorr.).[9] *Tert.*-amyl isothiocyanate was made in the same way through the amine, the latter having been prepared by the Hofmann reaction from dimethylethylacetamide. During the degradation of the amide, a considerable amount of a by-product melting at 224.5–225.5° was formed. Analysis proved this compound to be the symmetrical tertiary diamylurea. The tertiary-amyl isothiocyanate used in the tests boiled at 164–167°.[10]

[6] I. G. Farbenind. A.-G., French Patent 654,416, May 18, 1928, *Chem. Abstracts* **23,** 3770 (1929); I. G. Farbenind. A.-G. (Wilhelm Schepss and Wilhelm Bonrath, inventors), German Patent 484,995, Dec. 10, 1926; *Chem. Abstracts*, **24,** 1178 (1930); I. G. Farbenind. A.-G., British Patent 325,910, Dec. 12, 1928, *Chem. Abstracts*, **24,** 4116 (1930); I. G. Farbenind. A.-G. (Hans Kükenthal, Wilhelm Schepss and Carl Taube, inventors), German Patent 501,135, Nov. 16, 1928, *Chem. Abstracts*, **24,** 4578 (1930); I. G. Farbenind. A.-G. (Carl Taube and Hans Kükenthal, inventors), German Patent 506,085, Nov. 27, 1928, *Chem. Abstracts*, **25,** 373 (1931); Winthrop Chemical Co., Inc., U. S. Patent 1,794,046, Feb. 24, 1931 (Hans Wesche and Karl Brodersen, inventors), Review of U. S. Patents Relating to Pest Control (U. S. D. A. Bur. Chem. and Soils), Vol. IV, Nos. 2, 6 (Feb., 1931); Rohm and Haas Co., U. S. Patent 1,808,893, June 9, 1931 (Leon C. Heckert, inventor), *ibid.*, Vol. IV, Nos. 6, 1 (June, 1931); Winthrop Chemical Co., Inc., U. S. Patent 1,815,816, July, 21, 1931 (Hans Wesche and Karl Brodersen, inventors), *ibid.*, Vol. IV, Nos. 7, 6 (July, 1931).

[7] Gersdorff, THIS JOURNAL, **52,** 3440 (1930).

[8] Slotta and Dressler, *Ber.*, **63,** 889 (1930).

[9] The boiling point of *n*-amyl isothiocyanate is given in Beilstein, 4th ed., Vol. IV, p. 176, as 193.4° (corr.). Isoamyl isothiocyanate is not described in the literature.

[10] The boiling point reported in the literature is 166° at 770 mm. Beilstein 4th ed., Vol. IV, p. 179.

Benzoyl isothiocyanate was prepared from benzoyl chloride by the method described by Dixon and Taylor.[11] The fraction used boiled at 128–131° at 15 mm. pressure.

Phenyl thiocyanate was synthesized from aniline by means of the diazo reaction. The product boiled at 230–234°.[12]

p-Thiocyanogeno-N-dimethylaniline, melting at 71–73°, was also tested.[13]

Benzyl thiocyanate was made by the reaction between potassium thiocyanate and benzyl chloride. The substance used melted at 41–43°.[14]

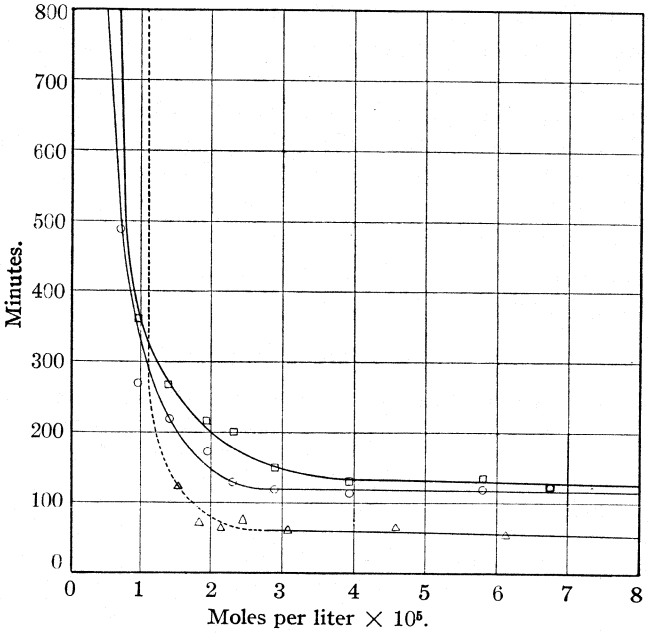


Fig. 1.—Survival time curves: ○, *n*-amyl isothiocyanate; □, isoamyl isothiocyanate; △, benzoyl isothiocyanate.

The Toxicity Tests

The acetone solutions of the substances to be tested were prepared at such concentrations that suitable aliquots could be taken for the tests without causing the proportion of acetone in the test jar to exceed 1 part in 1000 parts of water. Gersdorff[7] has shown that this concentration has no effect on goldfish.

[11] *J. Chem. Soc.*, **93**, 684 (1908). Dixon and Taylor found the boiling point of benzoyl isothiocyanate to be 119° at 10 mm.

[12] This product was kindly prepared by Mr. R. J. Busbey. The boiling point recorded in the literature for phenyl thiocyanate is 232–233°. Beilstein, 4th ed., Vol. VI, p. 312.

[13] Supplied by Dr. R. C. Roark of the Insecticide Division. This compound has been used in a commercial fly spray.

[14] Beilstein, 4th ed., Vol. IV, p. 460, records 36–38° for the melting point of this substance.

The time of addition of the solution to the test jars and the time of death of the fish were recorded. The survival times were then calculated. When an individual survival time differed widely from the others for the same concentration, the following test was applied[15] to see whether the result should be discarded in calculating the mean survival time. The mean survival time and the average deviation were calculated, omitting the doubtful observation. The difference between the doubtful observation and the mean was then found, and if this difference was equal to, or more than four times the average deviation, the questionable observation was rejected.

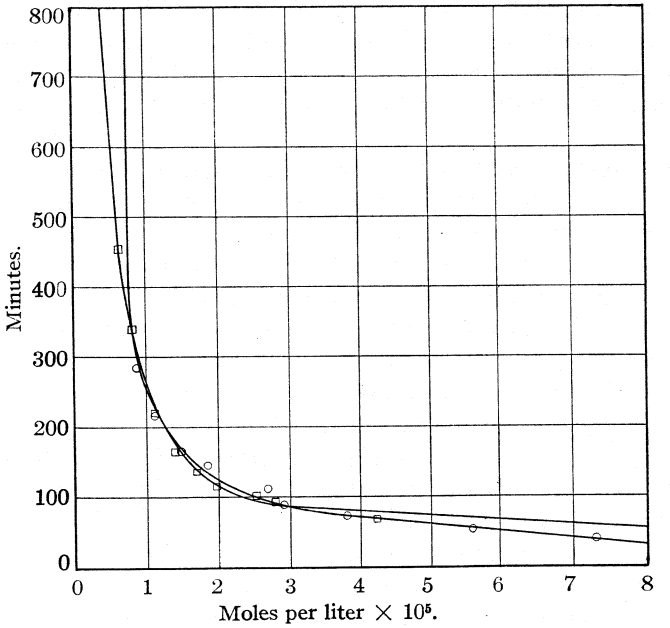


Fig. 2.—Survival time curves: ○, phenyl thiocyanate; □, *p*-thiocyanogeno-N-dimethylaniline.

As a general rule, six fish were used at each concentration, and after the mean survival time at different concentrations had been determined, the results were combined in the form of two graphs, shown in Figs. 1 and 2. Here are plotted survival times against concentration. The dotted portion of curve 3 of Fig. 1 is of questionable accuracy.

Discussion of Results

Examination of the curves reveals that except at the very low concentrations, the two amyl isothiocyanates are the least toxic. The other

[15] J. S. Stevens, "Theory of Measurements," D. Van Nostrand, New York, 1916, p. 71.

three compounds possess very nearly equal toxicity at high concentrations, but the toxicity of the benzoyl isothiocyanate falls off more rapidly than that of the other two substances after the curve begins to break from the horizontal. The curves of phenyl thiocyanate and of *p*-thiocyanogeno-N-dimethylaniline are very similar throughout their lengths, and the same holds true for the two amyl isothiocyanates. This result is to be expected, since the members of these two pairs are very similar chemically.

Isoamyl isothiocyanate is slightly less toxic than the corresponding *n*-amyl compound at all concentrations tested. Tertiary amyl isothiocyanate in concentrations of 2.90×10^{-5} mole/liter and 3.87×10^{-5} mole/liter had no effect on goldfish even though the fish were left in the solution overnight. As it was thought that possibly this isothiocyanate had decomposed on standing, a new sample was prepared and tested immediately. At concentrations of 3.88×10^{-5} and 3.48×10^{-5} mole/liter goldfish were unaffected.

The lack of toxicity of the tertiary amyl isothiocyanate and the decrease in toxicity in passing from *n*-amyl to isoamyl isothiocyanate are contrary to what one would expect judging from the work of Roark and Cotton.[5] Their fumigation tests indicated that among a group of isomers those with highly branched carbon chains were most effective. It is possible that this effect was the result of the higher vapor pressure of the branched chain isomers, since of a group of isomers the one with the most highly[16] branched chain invariably has the lowest boiling point.

In solutions containing 3.36, 5.60 and 7.38×10^{-5} mole/liter of benzyl thiocyanate goldfish showed no signs of distress after four hours. Tests with this substance were therefore discontinued, and no survival time curve for benzyl thiocyanate is given.

At the higher concentrations benzoyl isothiocyanate was much more toxic than the amyl compounds. Its toxicity diminished more rapidly, however, after the curve began to bend from the horizontal. At high concentrations of benzoyl isothiocyanate the survival times were nearly equal, but below concentrations of slightly less than 2×10^{-5} mole/liter erratic results were obtained. Repetition of the tests in this region gave results which differed widely, and when the concentration was diminished only a little more, all toxic effect disappeared. A large number of fish were used in obtaining each point in the vicinity of this break in the curve. The doubtful region is represented by a dotted line in Fig. 2.

The peculiar behavior of this substance is probably due to the fact that it is easily hydrolyzed in aqueous solution. In the more dilute solutions the odor of benzoyl isothiocyanate soon disappeared, but in the concentrated solutions a layer of undissolved isothiocyanate remained on top of the water and dissolved gradually. The odor of the substance per-

[16] Compared to the less highly branched isomers.

sisted for a long time in these solutions. It seems quite likely, therefore, that in the very dilute solutions the isothiocyanate decomposed too quickly to have any effect on the fish, while in the concentrated solutions the undissolved layers served as a reserve which kept benzoyl isothiocyanate in solution long enough to kill the goldfish. The fish which were killed by this compound bled from their gills, sometimes severely, and even those which did not die appeared inflamed about the gills.

At the higher concentrations, the toxicity of phenyl thiocyanate was very close to that of benzoyl isothiocyanate. Its decrease in toxicity became appreciable at a higher concentration than did that of benzoyl isothiocyanate, but the curve of Fig. 2 is regular, and results can be duplicated throughout its length. Phenyl thiocyanate is quite stable toward water. The goldfish were intensely irritated very quickly by this compound. They swam about violently, and often tried to jump out of the water.

p-Thiocyanogeno-N-dimethylaniline was very similar to phenyl thiocyanate in toxicity at all concentrations tested. It did not seem to irritate the fish as much as phenyl thiocyanate.

Summary

The toxicity to goldfish of certain organic thiocyanates and isothiocyanates has been determined at several concentrations, and the results are presented in the form of survival-time curves.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND STATION OF THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TWO CONSTITUENTS OF PAROSELA BARBATA (OERST.) RYDB.[1]

BY JOSEPH R. SPIES AND NATHAN L. DRAKE

RECEIVED MARCH 11, 1932 PUBLISHED JULY 6, 1932

Two constituents have been isolated from the leaves and stems of *Parosela barbata* (Oerst.) Rydb. in connection with the examination of certain plants reported to contain fish poisons.

The first, a white crystalline solid melting at 84–84.5°, was shown to be montanyl alcohol. This compound is assigned the formula $C_{29}H_{60}O$ by Damoy,[2] who obtained the alcohol from beeswax. Gascard and Damoy[3] report the melting point of montanyl alcohol as 84°. Damoy[2] gives the melting point of its acetate as 68–68.2° and that of its iodide as 64–64.2°.

On the other hand, Fargher and Probert[4] report montanyl alcohol ob-

[1] Collected by Dr. H. Pittier in Caracas, Venezuela, and identified by Dr. S. F. Blake, Bureau of Plant Industry, Washington, D. C.

[2] Damoy, *J. Pharm. Chim.*, **29**, 225–236 (1924).

[3] Gascard and Damoy, *Compt. rend.*, **177**, 1442–1443 (1923).

[4] Fargher and Probert, *J. Textile Inst.*, **15**, 337–346T (1924).

tained from the wax of American cotton as $C_{28}H_{58}O$ with a melting point of 83.5° and the melting point of its acetate as 67–67.5°.

The material isolated in this investigation was purified by repeated recrystallizations from chloroform until the melting point showed no further rise. The alcohol crystallizes from chloroform or benzene in colorless, diamond-shaped plates. It is very slightly soluble in cold solvents but is very soluble in warm chloroform or benzene. The highest yield of fairly pure substance was 0.075% of the plant and our total supply consisted of about 3.0 g.

Molecular weight determinations by the method of Landsberger[5] with chloroform as solvent gave values of 415, 412 and 385. By the method of Karl Rast[6] values of 410 and 387 were obtained.

The acetate of the material melted at 68–69° and the iodide melted at 64–64.5°. The phenylurethan was prepared and found to have a melting point of 96°. This derivative does not seem to have been prepared by previous workers.

It is not possible to distinguish positively between two compounds possessing formulas of $C_{28}H_{58}O$ or $C_{29}H_{60}O$ by means of carbon and hydrogen analysis due to the small difference in carbon and hydrogen content. There is, however, a difference of 0.62% in the iodine content of the two corresponding iodides, and analyses gave values which varied only 0.04 and 0.11% from the value calculated for $C_{29}H_{59}I$. This is in agreement with the formula for montanyl alcohol determined by Damoy.

The second constituent, a yellow oil, was obtained by steam distillation of the substance remaining after evaporation of the methyl alcohol mother liquor of the montanyl alcohol. The yield amounted to 0.6% of the plant material.

The oil boiled between 95 and 110° at 4–5 mm. pressure. Its density and refractive index were: d_{20}^{20} 0.947, and n_D^{20} 1.497. It possessed a peculiar sickening odor and was insoluble in water, but readily soluble in organic solvents. It added bromine readily and decolorized neutral permanganate solution but did not reduce Fehling's solution.

At a concentration of 1:10,000 at 27° it killed goldfish in an average of 117 minutes.[7] Four fish were used to obtain this value. The toxicity tests were carried out by the method described by Gersdorff.[8]

Experimental

Isolation of Montanyl Alcohol.—720 g. of the ground plant was extracted for two and a half hours in a Soxhlet extractor with benzene. The benzene was then dis-

[5] Landsberger, *Ber.*, **31**, 458 (1898).

[6] Karl Rast, *ibid.*, **55**, 1051 (1922).

[7] For toxicity of the acetone extract of the entire plant, see Drake and Spies, *J. Ec. Entomol.*, **25**, No. 1, 129–133 (1932).

[8] Gersdorff, THIS JOURNAL, **52**, 3440 (1930).

tilled off and the residue dissolved in boiling methyl alcohol and filtered on a hot water funnel. On cooling a gelatinous, green, pasty mass separated, which was filtered off with suction. This solid was stirred up with cold ether, which removed much of the color. The ether was filtered off, the solid dissolved in warm chloroform and the solution decolorized with charcoal. The chloroform solution was allowed to cool slowly and to stand for some time, whereupon it deposited a crystalline material which was further purified by repeated recrystallizations from the same solvent. A brownish color may persist even after this treatment, but it can be removed by a crystallization from methyl alcohol, followed by recrystallization from chloroform again; yield, 0.55 g. of substance melting at 82.5°. Recrystallization from chloroform to constant melting point gave a product melting at 84–84.5°.

Anal. Subs., 2.948, 2.919 mg.: CO_2, 8.813, 8.772; H_2O, 3.759, 3.687. Calcd. for $C_{28}H_{58}O$: C, 81.86; H, 14.24. Calcd. for $C_{29}H_{60}O$: C, 81.98; H, 14.25. Found: C, 81.53, 81.96; H, 14.17, 14.04.

Acetylation of Montanyl Alcohol.—0.15 g. of montanyl alcohol was treated with 2 cc.[9] of acetic anhydride containing a trace of sulfuric acid and kept on a boiling water-bath for one hour. Methyl alcohol was then added cautiously, and after destruction of the excess acetic anhydride the acetate crystallized from the methyl acetate–methyl alcohol mixture. The ester was recrystallized once more from methyl alcohol and melted at 68–69°.

Anal. Subs., 3.659, 3.262 mg.: CO_2, 10.680, 9.498; H_2O, 4.315, 3.901. Calcd. for $C_{30}H_{60}O_2$: C, 79.56; H, 13.36. Calcd. for $C_{31}H_{62}O_2$: C, 79.75; H, 13.39. Found: C, 79.60, 79.40; H, 13.10, 13.29.

Preparation of Montanyl Iodide.—0.09 g. of montanyl alcohol was treated with 0.025 g. of red phosphorus and 0.3 g. of iodine and the whole kept at a temperature of 80–90° for three and a half hours. The mixture was then extracted with warm chloroform and the chloroform solution washed with a dilute aqueous solution of sodium bisulfite. It was then washed with water and finally dried over calcium chloride. The chloroform was evaporated off and the solid residue recrystallized to constant melting point from ether. It melted at 64–64.5°.

Anal. Subs., 4.999, 3.205 mg.: CO_2, 11.856, 7.623; H_2O, 4.976, 3.207. Calcd. for $C_{28}H_{57}I$: C, 64.57; H, 11.04. Calcd. for $C_{29}H_{59}I$: C, 65.12; H, 11.13. Found: C, 64.67, 64.86; H, 11.06, 11.12. Subs., 6.907, 7.222 mg.: AgI, 3.052, 3.182. Calcd. for $C_{28}H_{57}I$: I, 24.39. Calcd. for $C_{29}H_{59}I$: I, 23.77. Found: I, 23.88, 23.81.

Preparation of the Phenylurethan of Montanyl Alcohol.—0.04 g. of montanyl alcohol and two drops of phenyl isocyanate were refluxed for half an hour in benzene solution. The crystals which separated on cooling were recrystallized once from benzene. The compound melted at 96°.

Anal. Subs., 2.874, 3.080 mg.: CO_2, 8.385, 8.971; H_2O, 3.136, 3.319. Calcd. for $C_{35}H_{63}O_2N$: C, 79.32; H, 11.99. Calcd. for $C_{36}H_{65}O_2N$: C, 79.48; H, 12.05. Found: C, 79.38, 79.41; H, 12.12, 11.97.

Summary

1. Montanyl alcohol has been isolated from *Parosela barbata* and identified by means of several of its derivatives.

2. The phenylurethan of montanyl alcohol has been prepared.

3. The formula of montanyl alcohol suggested by Damoy has been confirmed.

[9] This was sufficient to effect complete solution at 100°.

4. An oil possessing some toxicity to goldfish has been isolated and described.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

A REACTION BETWEEN DIETHYL ETHER AND PHOSPHORUS PENTACHLORIDE

BY WALTER S. GUTHMANN[1]

RECEIVED MARCH 11, 1932 PUBLISHED JULY 6, 1932

In the course of some work on molecular rearrangements in the triphenylmethylhydroxylamine series, it was found necessary to reflux ether solutions of the materials being studied with phosphorus pentachloride for several days. At the end of this time water was added to the reaction mixture, and a very considerable and unexpected evolution of acetaldehyde was observed. This led to the investigation reported here.

Liebermann and Landshoff[2] report the formation of a crystalline compound of the probable formula $C_8H_{14}O_2P_3Cl_{15}$, when ether is treated with phosphorus pentachloride, and show that it is not a direct addition product with the formula $(C_4H_{10}O)_2 \cdot 3PCl_5$. No mention is made, however, of the evolution of acetaldehyde upon addition of water to the above compound.

Reactions of phosphorus pentachloride with aliphatic–aromatic ethers have been reported.[3] In these cases only the aromatic portion of the molecule is oxidized.

It has been found that halogens, at ordinary temperatures, will react with ether to form α-halogen ethyl ethers which are easily hydrolyzed by water:[4]

$$CH_3CHClOCH_2CH_3 + HOH \longrightarrow CH_3CH_2OH + CH_3CHO + HCl$$[5]

It is well known that phosphorus pentachloride may be used as a chlorinating agent, and this fact might well account for the reaction described below, except that some organic phosphorus derivatives are formed at the

[1] A portion of the dissertation submitted to the graduate faculty of the University of Chicago, by W. S. Guthmann, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Liebermann and Landshoff, *Ber.*, **13**, 690 (1880).

[3] Henri, *ibid.*, **2**, 710 (1869); Colson, *Compt. rend.*, **99**, 975 (1884).

[4] Richter, "Organic Chemistry," P. Blakiston's Son and Co., Philadelphia, 1922, Vol. I, p. 129.

[5] Since this paper was written, Henze and Murchison [THIS JOURNAL, **53**, 4077 (1931)], have reported the preparation of α-chloroethyl *n*-alkyl ethers by saturating equimolar quantities of paraldehyde, and the alcohol which contains the desired alkyl group, with hydrogen chloride, in the cold. The products hydrolyze very readily to re-form the original materials; on long standing they polymerize and leave a dark tarry residue.

same time (see experimental part). We might accept the point of view of Bergmann and Bondi,[6] who advance evidence that one of the five chlorine atoms in phosphorus pentachloride is differently and less firmly linked than the others, which causes this compound to react as $Cl–PCl_4$; this would account for a C–P linkage in the product of reaction of phosphorus pentachloride with an organic compound.

The ultimate reaction product of phosphorus pentachloride with ether is an oil, not completely miscible with ether, and perfectly stable, at room temperatures, in the absence of moisture. All attempts to crystallize it have failed. On treatment with water the oil yields acetaldehyde, hydrochloric, phosphoric and phosphorous acids, and an unidentified organic residue which contains trivalent phosphorus. In view of the fact that the oil is most probably a mixture, no elementary analysis has been attempted. It is possible that this reaction provides an additional method for the preparation of the type of phosphoric and phosphorous esters prepared by Milobdendzki and Sachnowski[7] and by Arbuzov and Arbuzuva.[8]

Further work in this field should yield valuable information on organic phosphorus compounds, and conceivably serve to develop a method for the determination of the relative ease of oxidation of the groups in mixed ethers.

Experimental Part

A mixture of pulverized phosphorus pentachloride (7 g.) and ether (30 cc.), carefully dried and purified, was boiled under reflux[9] on the steam-bath for forty-eight hours, the reaction mixture being protected from moisture by means of a calcium chloride tube. At the end of this time a clear, almost colorless, mobile solution resulted. The reaction flask was well cooled and agitated while water (75 cc.) was slowly added to its contents. After separation from the aqueous layer, the ether layer was repeatedly washed with water. The washings were added to the original aqueous part. The presence of some organic phosphorous compound in the ether layer was shown as follows: the solution was dried over calcium chloride (or potassium carbonate), the solvent evaporated, and the residue oxidized with concentrated nitric acid; addition of molybdic acid then gave a precipitate, although no such precipitate was obtained prior to the oxidation.[10]

---

[6] Bergmann and Bondi, *Ber.*, **64B**, 1455–80(1931).

[7] Milobdendzki and Sachnowski, *Chem. Polski*, **15**, 34 (1917); *cf. Chem. Abs.*, **13**, 2865 (1919).

[8] Arbuzov and Arbuzuva, *J. Russ. Phys.-Chem. Soc.*, **62**, 1533 (1930); *cf. Chem. Abs.*, **25**, 2414 (1931).

[9] The flasks used here were of 150-cc. capacity, and were joined to the condenser by means of a ground-glass joint in such a way that the condensed liquid washed the solid material (which otherwise tends to cake on the walls just above the surface of the reaction mixture) back into the bottom of the flask. These flasks also have the great advantage that contamination of the reaction mixture from stoppers is prevented.

[10] Evaporation of the ether, prior to the hydrolysis, left an oil which did not crystallize on standing. Hydrolysis of this oil yielded the same products that were obtained from the ethereal solution.

The aqueous portion was fractionated; the fraction boiling below 35° contained all the acetaldehyde, which was identified by one of its many color reactions, and also by the preparation of the aldehyde semicarbazone[11] (melting point 162°). A mixture of the latter material with acetaldehyde semicarbazone from a known source had the same melting point (162°).

The distillation of the aqueous layer was continued until the volume of the material in the flask was reduced one-half; this residue was used for the following tests. (1) A portion allowed to stand exposed to air acquired a brown coloration, but no other change in properties was noted. (2) The presence of phosphate ion was shown by the molybdic acid reaction and confirmed by the precipitation of magnesium ammonium phosphate. When bromine was added to the filtrate obtained in the molybdic acid test, the yellow liquid became colorless, and some of the phosphorus was oxidized to phosphate ion, as was shown by the formation of more precipitate, an excess of molybdic acid having previously been used. (3) Ferric chloride was added to another portion, and the resulting mixture was made slightly alkaline and filtered. Addition of molybdic acid to a portion of the filtrate now gave no precipitate; but when another portion of the filtrate was oxidized with bromine or with concentrated nitric acid, the test for phosphate ion was positive.

The phosphate-free solution mentioned above has strong reducing properties when alkaline. It also gives the various tests for phosphorous acid, and we have the following indications of an organo-phosphorus compound: when the neutralized solution was evaporated a brown sirup resulted, encrusted with sodium chloride (formed in the neutralization of the hydrochloric acid originally present). This brown sirup was further heated, and first gave phosphine (identified in the usual way), and later became charred with the production of a distinct carbylamine odor, although no nitrogen was present. The residue which remained after the heating, when extracted with water, gave the usual phosphate tests; much carbon remained.

I wish to take this opportunity to express my sincere gratitude to Professor Stieglitz for his kind help and guidance.

Summary

1. A new reaction of diethyl ether and phosphorus pentachloride is described.

2. Organo-phosphorus compounds are formed in the course of the reaction. These are easily hydrolyzed by water alone.

3. The products of hydrolysis of the compounds mentioned in (2) include acetaldehyde, hydrogen chloride, phosphoric and phosphorous acids, and some unidentified stable organo-phosphorus compounds.

CHICAGO, ILLINOIS

[11] Thiele and Bailey, *Ann.*, **303**, 79 (1898).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXXIX. THE SYNTHESIS OF 2-THIO-OROTIC ACID

BY TREAT B. JOHNSON AND ELMER F. SCHROEDER[1]

RECEIVED MARCH 12, 1932 PUBLISHED JULY 6, 1932

The two sulfur analogs of uracil-4-carboxylic acid (orotic acid)[2] and uracil-5-carboxylic acid,[3] respectively, have been described in the chemical literature. The pyrimidine acid represented by formula II was synthesized

NHCSNHCOCHC(COOH) NHCSNHCOC(COOH)CH

I II

by Johnson and Ambler[4] in 1911, and the isomeric acid I by Bachstez[5] in 1930. Both of these pyrimidines have a biochemical interest, and the presence of sulfur in the molecule increases greatly the possible application of these two compounds for future synthetic operations.

Bachstez's method of preparing 2-thio-orotic acid involves the condensation of thiourea with ethyl oxaloacetate to form the ethyl ester of 2-thio-orotic acid, which is then converted into the acid I by saponification. In other words, practically the same technique is employed here for its preparation as was originally applied by Müller for the synthesis of the ethyl ester of uracil-4-carboxylic acid. Neither condensation reaction is productive of pyrimidines in good yield, that reported by Bachstez for 2-thio-orotic acid averaging, for example, less than 21% of the theoretical.

In the progress of our researches on pyrimidines we have sought for an improved method of preparing 2-thio-orotic acid, and find that it can be prepared easily by application of a Cannizzaro reaction to the corresponding pyrimidine aldehyde, 2-thiouracil-4-aldehyde. This aldehyde and also the corresponding uracil-4-aldehyde have been described previously in papers by Johnson and Cretcher[6] and by Johnson and Schroeder.[7] Both pyrimidines undergo smoothly a Cannizzaro transformation, giving practically quantitative yields of the corresponding pyrimidine acids and primary alcohols as is expressed below

1. 2-Thiouracil-4-aldehyde ⟶ 2-thio-orotic acid and 2-thio-4-hydroxymethyluracil.
2. Uracil-4-aldehyde ⟶ orotic acid and 4-hydroxymethyluracil.

These transformations (1 and 2) not only illustrate the importance of our original pyrimidine aldehyde syntheses, but they also introduce

[1] Sterling Research Assistant in Chemistry, 1930.

[2] Wheeler, *Am. Chem. J.*, **38**, 358 (1908); Müller, *J. prakt. Chem.*, **56**, 488 (1897).

[3] Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 392 (1907).

[4] Johnson and Ambler, THIS JOURNAL, **33**, 982 (1911).

[5] Bachstez, *Ber.*, **64**, 322 (1930).

[6] Johnson and Cretcher, THIS JOURNAL, **37**, 2144 (1915).

[7] Johnson and Schroeder, *ibid.*, **53**, 1989 (1931).

workers in this field to a method for synthesizing primary alcohol derivatives of uracil, which is an improvement over the method previously developed in this Laboratory. Both 2-thio-orotic acid and the corresponding 2-thio-4-hydroxymethyluracil can be converted quantitatively into orotic acid and 4-hydroxymethyluracil, respectively, by desulfurization.

In his last publication on the chemistry of 2-thio-orotic acid, Bachstez discusses the behavior of the sodium salt of this acid toward benzyl chloride, and describes the reaction product, melting at 264°, as a N-benzyl derivative. It has been our experience that the sodium salt of 2-thio-orotic acid and also 2-thio-4-hydroxymethyluracil interact with alkyl halides to form smoothly alkyl derivatives with the substituent group attached to sulfur. Several representatives of this type of derivative have been prepared by us, and we have observed that they undergo hydrolysis by acids, in every case examined, with formation of mercaptans and the corresponding sulfur-free pyrimidines. In other words, no abnormality in behavior is revealed in this series of compounds.

Experimental Part

The Application of Cannizzaro's Reaction to 2-Thiouracil-4-aldehyde.[6,7] The Preparation of 2-Thio-orotic Acid and 2-Thio-4-hydroxymethyluracil.—Five grams of 2-thiouracil-4-aldehyde is dissolved in a solution of 5 g. of potassium hydroxide and 12 cc. of water, previously cooled to room temperature. The aldehyde dissolves readily with rise in temperature to give a clear bright red solution. The reaction is practically complete after standing at room temperature for forty-eight hours.

The reaction mixture is then acidified with dilute hydrochloric acid and the precipitate, consisting of both reaction products, is separated by filtration, suspended in 50 cc. of water and redissolved by addition of a small amount of sodium hydroxide solution. On acidifying this solution with acetic acid the 2-thio-4-hydroxymethyluracil is precipitated in crystalline condition, and the separation is usually complete within half an hour. This alcohol is easily purified by crystallization from hot water, and separates on cooling in the form of colorless needles. The yield was 1.8 g. This pyrimidine is moderately soluble in hot alcohol, easily soluble in concentrated sulfuric acid and hot acetic acid, and insoluble in ether, benzene, ligroin and acetone. It melts with decomposition at 259°.

Anal. Calcd. for $C_5H_6O_2N_2S$: N, 17.72. Found: N, 17.66, 17.70.

The filtrate from the acetic acid precipitation is then made strongly acid with hydrochloric acid when the 2-thio-orotic acid is precipitated as a yellow powder. The yield was 2.4 g. This pyrimidine was purified by repeated reprecipitations from alkaline solution with hydrochloric acid. It does not show a sharp melting point and decomposes with strong effervescence when heated at 338–339°. The acid described by Bachstez[5] showed a similar behavior, melting at the same temperature. This pyrimidine is very insoluble in cold water, alcohol and ether, but is moderately soluble in hot water.

Anal. Calcd. for $C_5H_4O_3N_2S$: N, 16.28. Found: N, 16.30, 16.43.

Conversion of 2-Thio-orotic Acid into Orotic Acid.—The desulfurization of 2-thio-orotic acid is accomplished quantitatively by oxidation with chromic acid. Two grams of the sulfo acid is slowly added to an oxidizing mixture consisting of 5 g. of sodium dichromate, 5 cc. of sulfuric acid and 25 cc. of water. Considerable heat is evolved during the addition. After standing for a short time, the reaction mixture is heated to

boiling for about one minute. On cooling, the sulfur-free orotic acid separates out as a yellowish solid. It is decolorized with norite and recrystallized from hot water. The purified product melted at 345°. A mixed melting point with known orotic acid showed no depression; yield, 1.9 g.

The desulfurization may also be accomplished by heating for a short time with alkaline 3% hydrogen peroxide. Two grams of 2-thio-orotic acid is covered with 25 cc. of 3% hydrogen peroxide and sufficient sodium hydroxide solution is added to dissolve the acid. The solution is heated to a gentle boil for three minutes. On cooling and acidifying with hydrochloric acid, the orotic acid separates out as a colorless solid. The yield was 1.8 g. Attempts to desulfurize 2-thio-orotic acid with monochloroacetic acid were not successful.

Conversion of 2-Thio-4-hydroxymethyluracil into 4-Hydroxymethyluracil.—Two grams of 2-thio-4-hydroxymethyluracil is suspended in a solution of two grams of monochloroacetic acid in 25 cc. of water. The pyrimidine readily goes into solution on warming. The solution is heated under a reflux condenser for five hours, remaining perfectly clear during this period. On cooling, 4-hydroxymethyluracil separates out in the form of colorless elongated prisms or plates. It may be purified by recrystallization from a small quantity of hot water; yield, 1.5 g. The product darkened at 248° and then melted sharply at 255–256°. It gave no test for sulfur. It was easily soluble in hot water, acetic acid, methyl and ethyl alcohol, and insoluble in ether and benzene.

Anal. Calcd. for $C_5H_6O_3N_2$: N, 19.72. Found: N, 19.52, 19.65.

4-Hydroxymethyluracil was first prepared by Johnson and Chernoff[8] by way of the intermediate, 4-ethoxymethyluracil. The product which they obtained did not melt sharply, showing signs of decomposition at 240° then melting at 254°.

Application of the Cannizzaro Reaction to Uracil-4-aldehyde.—Uracil-4-aldehyde undergoes a Cannizzaro reaction when allowed to stand in aqueous potassium hydroxide solution to give orotic acid and 4-hydroxymethyluracil. Five grams of the aldehyde, prepared according to the method of Johnson and Schroeder[7] is dissolved in a solution of 8 g. of potassium hydroxide and 18 cc. of water, and allowed to stand at room temperature for forty-eight hours. The solution assumes a deep yellow color and partially solidifies. At the end of the reaction 25 cc. of water is added and the solution then acidified with concentrated hydrochloric acid, cooled in ice water, and the yellowish precipitated mixture of alcohol and acid filtered off by suction.

The separation of the two reaction products depends on the much greater solubility of the pyrimidine alcohol in hot water. The precipitate obtained as described above is transferred to a beaker, covered with 50 cc. of water and heated nearly to boiling (85–90°). Practically the whole of the pyrimidine alcohol goes into solution, while if the heating is not continued too long, only negligible amounts of orotic acid dissolve. The mixture is rapidly filtered hot, and the extraction of the solid residue is repeated in the same way, using 25 cc. of water. The crude yellow residue of orotic acid is purified with norite and recrystallized from hot water, from which it separates in colorless rhombic blocks; yield, 2.0 g. It melted at 345°. A mixed melting point with known orotic acid showed no depression.

The alcohol, 4-hydroxymethyluracil, is obtained on concentrating and cooling the extraction liquors. It is purified with norite and recrystallized from a small quantity of hot water, separating in the form of colorless elongated prisms or plates, melting at 255–256°. A mixed melting point with the product previously described, obtained by desulfurization of 2-thio-4-hydroxymethyluracil, showed no depression, melting at 255°; yield, 1.6 g.

[8] Johnson and Chernoff, THIS JOURNAL, **36**, 1742 (1914).

2-Ethylmercapto-4-hydroxymethyluracil (A) and 2-Benzylmercapto-4-hydroxymethyluracil (B).—These two pyrimidines are easily prepared by alkylation of the sodium salt of 2-thio-4-hydroxymethyluracil with ethyl iodide and benzyl chloride, respectively, in alcohol solution. Practically quantitative yields of the mercapto pyrimidines are obtained. The pyrimidine (A) melts at 168°. It is easily soluble in alcohol, acetone and acetic acid, and slightly soluble in ether and benzene. When digested with hydrochloric acid ethyl mercaptan is evolved and 4-hydroxymethyluracil is formed, melting at 255°.

Anal. Calcd. for $C_7H_{10}O_2N_2S$: N, 15.05. Found: N, 15.14, 15.08.

The benzyl derivative (B) crystallizes from hot water in the form of needles melting at 156°. This pyrimidine is easily soluble in alcohol, acetone and acetic acid, and insoluble in ether and benzene. When digested with hydrochloric acid benzyl mercaptan and 4-hydroxymethyluracil are formed.

Anal. Calcd. for $C_{12}H_{12}O_2N_2S$: N, 11.29. Found: N, 11.18, 11.22.

2-Benzylmercapto-orotic Acid (A). 2-Ethylmercapto-orotic Acid (B) and 2-Methylmercapto-orotic Acid (C).—(A) This pyrimidine was prepared by the following modification of the method employed by Bachstez. Two grams of thio-orotic acid was dissolved in a solution of 1.3 g. of potassium hydroxide (two mols) in 24 cc. of an 80% alcohol–water mixture, and refluxed for three hours with 1.5 g. of benzyl chloride (one mol). At the end of this time the reaction mixture was diluted with 200 cc. of water and acidified with hydrochloric acid. The white solid separating out was recrystallized from a large quantity of hot water and came out in the form of small colorless prisms melting at 265° (corr.). Bachstez reports a melting point of 264° (corr.). The yield was 1.8 g. The product was difficultly soluble in alcohol and ether.

The structure of this compound is erroneously reported by Bachstez to be that of a N-benzyl-2-thio-orotic acid, the benzyl group being linked to one of the nitrogen atoms in the pyrimidine cycle. That the benzyl group is in fact linked to sulfur is shown by the ready conversion of the compound in question to orotic acid, with loss of benzyl mercaptan. A small amount of 2-benzylmercapto-orotic acid is dissolved in concentrated hydrochloric acid and refluxed for six hours. A strong mercaptan-like odor appears. On evaporating the solution to dryness and extracting the residue with hot water, a good yield of orotic acid is obtained.

(B) This pyrimidine is prepared by the action of ethyl bromide on the sodium salt of thio-orotic acid in alcohol solution. The pyrimidine is easily purified by recrystallization from hot water and separates on cooling in the form of colorless prisms melting at 248°. It is easily soluble in hot water and alcohol and insoluble in ether and benzene. When the pyrimidine was digested with hydrochloric acid ethyl mercaptan and orotic acid were formed quantitatively.

Anal. Calcd. for $C_7H_8O_3N_2S$: N, 14.00. Found: N, 13.92.

(C) This pyrimidine crystallizes from hot water in the form of prisms melting at 255°. It is converted quantitatively into orotic acid with evolution of methyl mercaptan when digested with hydrochloric acid.

Anal. Calcd. for $C_6H_6O_3N_2S$: N, 15.05. Found: N, 15.09.

Summary

1. The pyrimidine aldehyde, 2-thiouracil-4-aldehyde and uracil-4-aldehyde react normally toward alkali and undergo the Cannizzaro reaction, giving equivalent amounts of the corresponding pyrimidine acid and alcohol.

2. 2-Thio-orotic acid is desulfurized by the action of chromic acid, or with hydrogen peroxide in alkaline solution to give orotic acid quantitatively. The acid is not desulfurized by the action of chloroacetic acid.

3. 2-Thio-4-hydroxymethyluracil is desulfurized and converted quantitatively into 4-hydroxymethyluracil by digestion with chloroacetic acid in aqueous solution.

4. 2-Thio-orotic acid and 2-thio-4-hydroxymethyluracil interact with alkyl halides in alkaline solution to give alkyl derivatives with substitution on the sulfur atom.

5. The investigation of these compounds is being continued.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

SUBSTITUTED PHENYLDIHALOARSINES

BY F. F. BLICKE, L. D. POWERS AND G. L. WEBSTER

RECEIVED MARCH 12, 1932 PUBLISHED JULY 6, 1932

A number of substituted phenyldihaloarsines, not described hitherto, have been prepared in the hope that they might be used for the preparation of certain types of arsenicals under investigation in this Laboratory. Since many of them have been found to be unsuitable for our purpose, a brief description of them is published at this time.

Considerable difficulty was experienced in the preparation of many of the dihaloarsines in pure form. The following was found to be a very satisfactory general procedure: preparation of the arylarsonic acid, conversion of the acid into the corresponding aryldichloroarsine, purification of the latter by recrystallization from acetic acid or absolute ether, hydrolysis of the chloride into the arylarsine oxide and treatment of the latter at ordinary temperature with the desired halogen acid.

Arylarsine oxides are sometimes contaminated by small quantities of the arylarsonic acid and as a result of this contamination the preparation of the aryldihaloarsine is often very troublesome. Since the pure oxides usually possess rather indefinite melting points, the detection of the arsonic acid by means of a melting point determination cannot be relied upon. However, since the arylarsonic acid and concentrated hydriodic acid yield the corresponding aryldi-iodoarsine and free iodine, it is merely necessary to add a cubic centimeter of hydriodic acid to a fraction of a gram of the solid oxide in order to determine the presence or absence of the arsonic acid. If the oxide is pure, the mixture assumes the yellow color of the aryldi-iodoarsine; if even a slight amount of arsonic acid is present, the latter is detected by a deep red color due to the free iodine.

Experimental Part

TABLE I

SUBSTITUTED PHENYLDICHLOROARSINES

	M. p., °C.	Formulas	Chlorine analyses[a] Calcd.	Found
3-Nitro	53–54[b]	$C_6H_4O_2NAsCl_2$	26.47	26.36
4-Benzoyl	118–120	$C_{13}H_9OAsCl_2$	21.69	21.65
4-(4′-Phenoxy)-benzoyl	83–85	$C_{19}H_{13}O_2AsCl_2$	16.92	16.61

[a] All halogen analyses were made by the use of the Thompson–Oakdale method, THIS JOURNAL, **52,** 1195 (1930). Oxidation was effected with chromic acid.

[b] Michaelis and Loesner [*Ber.*, **27,** 269 (1894)] reported the melting point to be 46–47°.

TABLE II

SUBSTITUTED PHENYLDIBROMOARSINES

	M. p., °C.	Formulas	Bromine analyses Calcd.	Found
2-Nitro	52–54	$C_6H_4O_2NAsBr_2$	44.79	44.91
3-Nitro	63–64	$C_6H_4O_2NAsBr_2$	44.79	44.69
2-Iodo	71–72	$C_6H_4AsBr_2I$[a]	28.99	28.69
2-Methoxy	84–85	$C_7H_7OAsBr_2$	46.75	46.54
4-Methoxy	40–41	$C_7H_7OAsBr_2$	46.75	46.84
4-Carboxy	161–162	$C_7H_5O_2AsBr_2$	44.91	44.81
4-Benzoyl	116–118	$C_{13}H_9OAsBr_2$	36.91	36.80
4-(4′-Phenoxy)-benzoyl	105–106	$C_{19}H_{13}O_2AsBr_2$	31.47	31.07

[a] Calcd. for $C_6H_4AsBr_2I$: As, 17.12. Found: As, 17.16.

In general acetic acid was found to be the most satisfactory solvent from which to recrystallize the dihaloarsines; absolute ether was used in a few instances.

TABLE III

SUBSTITUTED PHENYLDI-IODOARSINES

	M. p., °C.	Formulas	Iodine analyses Calcd.	Found
2-Nitro	83–84	$C_6H_4O_2NAsI_2$	56.30	56.08
3-Nitro	64–65	$C_6H_4O_2NAsI_2$	56.30	56.49
2-Iodo	97–98	$C_6H_4AsI_3$	71.47	71.63
2-Methoxy	74–76	$C_7H_7OAsI_2$	58.24	58.43
4-Methoxy	38–40	$C_7H_7OAsI_2$	58.24	58.31
2-Benzoyl	115–117	$C_{13}H_9OAsI_2$	49.78	49.59
4-Benzoyl	92–93	$C_{13}H_9OAsI_2$	49.78	49.81
4-(4′-Phenoxy)-benzoyl	127–128	$C_{19}H_{13}O_2AsI_2$	42.17	41.94

The melting point of 4-carboxyphenyldi-iodoarsine was reported to be 153° by La Coste [*Ann.*, **208,** 13 (1881)] and 172° by Bertheim [*Ber.*, **41,** 1857 (1908)]; we found the melting point to be 168–169°.

Lewis and Cheetham [THIS JOURNAL, **45,** 514 (1923)] stated that 4-(4′-methoxy)-benzoylphenyldi-iodoarsine melts at 105°, while we observed the melting point to be 110–111°.

Summary

The preparation of a number of new substituted phenyldihaloarsines has been described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

SALTS OF PHENOLPHTHALEIN

BY WILLIAM M. DEHN

RECEIVED MARCH 14, 1932 PUBLISHED JULY 6, 1932

The problem of constitution of the salts[1] of phenolphthalein has engaged the interest of many chemists since 1871, the date of discovery by Baeyer[2] of free phenolphthalein, which later he showed[3] possesses the lactone structure. The exact constitution of its salts, the reddening and fading effects produced by a variety of influences, and the correlations of chemical and color changes in solutions have been the chief problems giving rise to different opinions.

It is usually suggested that the color changes of phenolphthalein are in accordance with equilibrium of the following forms[4]

$$\text{Colorless lactone} \rightleftharpoons \text{red quinoid} \rightleftharpoons \text{colorless carbinol}$$

However, since the solid colorless mono-, di- and tri-basic salts all yield by dehydration corresponding red salts, it seems probable that more than one colored quinoid form and colorless carbinol forms are involved in equilibria both of the solid salts and in their solutions. Furthermore, no structures depict water of crystallization, which is always present in the colorless salts and in some of the red salts, and it seems certain that equilibria of such water molecules are involved in solutions, at least in saturated solutions, as well as in the dry salts. Then, too, it must be remembered, whereas isomerization, neutralization, hydrolysis, hydration and de-

[1] Only a few salts have hitherto been prepared, namely, salts of sodium, potassium, calcium and silver, and these possess different colors. The dry hydrated salts of sodium and potassium are colorless and their anhydrous salts are red. The silver salt is red. Red and green salts of calcium were described by Meyer and Posner, *Ber.* **44,** 1954 (1911). See experimental part of this paper.

[2] Baeyer, *Ber.*, **4,** 659 (1871).

[3] Baeyer, *Ann.*, **202,** 36 (1880).

[4] Apparently Bernthsen was the first to use the quinoid formula in connection with phenolphthalein, *Chem.-Ztg.*, **16,** 1956 (1892). Also see Dehnst, *ibid.*, **17,** 654 (1893); Friedländer, *Ber.*, **26,** 172 (1893); Armstrong, *Proc. Roy. Soc.* (London), 55 (1893). For opinions of the non-existence of the quinoid form for phenolphthalein, see Hjelt, *Chem.-Ztg.*, **18,** 3 (1894); Herzig and Meyer, *Ber.*, **29,** 138 (1896); Bistrzyski and Nencki, *ibid.*, **29,** 131 (1896); Schestakov and Nocken, *ibid.*, **47,** 331 (1914); Oddo, *ibid.*, **47,** 967 (1914); Consonno and Apostolo, *Gazz. chim. ital.*, **51,** [1] 50 (1921).

hydration are all probably involved, there are at least eight color-changing *first causes*.[5]

Experimental

Methods of Formation of Salts of Phenolphthalein.—Owing to the great solubilities of salts of phenolphthalein in organic solvents, the insolubility of most inorganic bases and the capacity of phenolphthalein to form a series of salts with the same base, a variety of methods must be employed to obtain the different salts. The following methods were effective. (a) A metal, such as sodium, was dissolved in an alcohol, phenol, or ketone, and the resulting sodium compound was treated in the presence of the excess of the solvent, with the calculated quantity of phenolphthalein. On standing, the salt usually crystallized out. Promotion of formation of the red salts was influenced by the absence of water in the solvent. If the white hydrated salt was desired, usually a little water was added. The white salts were filtered off, washed with a little alcohol or methyl ethyl ketone, and dried in the desiccator. Whether or not an alkali alcoholate, etc., was first formed, the added water always was found to have formed the hydrated salts, free from combined alcohol, phenol or ketone.

(b) Solid hydrates were added to solutions of the phenolphthalein. These solids were gradually replaced by the solid salts. For the alkali metals, an organic solvent was used; for the alkali-earth metals, water was used. The latter salts could be formed very slowly in ordinary alcohol.

(c) The sodium or better the ammonium salt of phenolphthalein was treated with the acetate of the metal. When the heat of formation of the latter is less than that of the alkali acetate, the new salt of phenolphthalein can be formed.

(d) An ammoniacal solution of the base was treated with an ammoniacal or with an alcohol solution of phenolphthalein.

Ammonium Salt.—Anhydrous ammonia was passed into a mixture of methyl

[5] COLORING. *By acids*, such as HCl, $HClO_4$, etc., Meyer and Hantzsch, *Ber.*, **40**, 3482 (1907); Hofmann and Keimreuter, *ibid.*, **42**, 4856 (1909). *By alkalies*. Baeyer, *loc. cit.* *By water*. All colorless salts dissolve in water to give colored solutions. *By heat*. Herzig and Meyer, *Ber.*, **28**, 3258 (1895); **29**, 138 (1896); Green and Perkin, *J. Chem. Soc.*, **85**, 398 (1904). *By certain salts*, such as $AlCl_3$, $SnCl_4$, etc., Meyer and Hantzsch.[4] *By alcohol*, Meyer and Marx, *Ber.*, **40**, 3603 (1907). They prepared red alkali salts in absolute alcohol. *By pressure*. Oddo and Vassallo, *Gazz. chim. ital.*, **42**, 209 (1912). *By friction*. All white salts prepared in this paper were reddened by rubbing with a glass rod.

BLANCHING. *By acids*. Green and Perkin observed that neutralization by acetic acid of strongly alkaline solution in potassium hydroxide yielded unstable colorless $C_{20}H_{15}O_5K$. *By more alkali*. Baeyer.[2,3] Menschutkin, *Ber.*, **16**, 315 (1883); Green and Perkin, above; Jones and Allen, *Am. Chem. J.*, **18**, 377 (1896); Hildebrand, THIS JOURNAL, **30**, 1914 (1908); Wegscheider, *Z. physik. Chem.*, **100**, 532 (1922). *By water*, McCoy, *Am. Chem. J.*, **31**, 520 (1904). *By cooling*. Meyer and Hantzsch, above. *By salts*, such as Na_2CO_3, Sztankay and Geyer, *J. Soc. Chem. Ind.*, **34**, 1167 (1915), German Patent 286,020. *By alcohol*. Draper and Draper, *Chem. News*, **55**, 133, 143 (1887); McCoy, *loc. cit.*; Schmatolla, *Ber.*, **35**, 1905 (1904); Jones and Allen, *Am. Chem. J.*, **18**, 377 (1896), explain the phenomena on the basis of suppression of the hydroxyl ions. Hildebrand, THIS JOURNAL, **30**, 1914 (1908), concludes that the alcohol unites with the phenolphthalein. Wegscheider, *Z. physik. Chem.*, **100**, 532 (1922), concurs in this opinion. Since red salts can be prepared in absolute alcohol and since colorless salts can be prepared in ordinary alcohol, it is evident that the concentration of water contained therein makes the difference.

ethyl ketone and phenolphthalein until the latter dissolved. On evaporating spontaneously in a desiccator over sulfuric acid, white crystals were obtained.

Anal. Calcd. for $C_{20}H_{14}O_4 \cdot NH_4OH$: NH_4OH, 9.51. Found (loss on heating to 130°): NH_4OH, 9.92.

White Monopotassium Phenolphthalein.[6]—Prepared in methyl ethyl ketone from equivalent quantities of potassium hydroxide and phenolphthalein, glistening white rectangular plates and prisms, with truncated corners and beveled ends, were obtained.

Anal. Calcd. for $C_{20}H_{14}O_4 \cdot KOH \cdot 2H_2O$: H_2O, 13.17; K, 9.55. Found: H_2O, 13.12; K, 9.35.

This compound was also prepared from potassium cyanide. When its mixture with phenolphthalein in methyl ethyl ketone was permitted to stand for days, no precipitate formed. When a little water was added, an immediate voluminous precipitate of the above salt was obtained. Here either the cyanide was first added to phenolphthalein and the product was then hydrolyzed or the cyanide was first hydrolyzed and the potassium hydroxide then added.

Red Monopotassium Phenolphthalein.—A hot concentrated solution of equivalent quantities of potassium hydroxide and phenolphthalein in 95% alcohol was treated with a little ether and then was permitted to stand. After a few minutes there were formed rosets of red needles and long rectangular leaflets which were blanched by ether and rereddened by ordinary alcohol.

Anal. Calcd. for $C_{20}H_{14}O_4 \cdot KOH \cdot H_2O$: water, 9.18; K, 9.96. Found: water, 9.11; K, 10.01.

Red Disodium Salts.—The sodium hydroxide was prepared by Cornog's[7] or by Kuster's[8] method. For example, the necessary weight of sodium was dissolved in amyl alcohol and this mixture was treated with the calculated weight of phenolphthalein. On adding anhydrous ether to this deep red solution, little or no precipitate formed but the solution became indigo-violet by transmitted light. On adding water to this ether solution in quantities necessary for forming the hydrated salt, a voluminous red precipitate was obtained.

Anal. Calcd. for $C_{20}H_{12}O_4Na_2 \cdot 2H_2O$: H_2O, 9.05; Na, 11.55. Found: H_2O, 9.76; Na, 11.30.

Contact with atmospheric moisture slowly changed this color through lighter reds to white.

Red Calcium Salt.—This was prepared by Meyer and Posner by quite an involved method. It is easily prepared by treating freshly ignited marble with phenolphthalein in the presence of a little water. Its composition was given as $C_{20}H_{12}O_4Ca \cdot 2.5H_2O$; its more probable composition is $C_{20}H_{14}O_5Ca \cdot 2H_2O$, whose structural relations can be in-

[6] Kober and co-workers obtained the colorless monopotassium salt containing 1 mole of water and 1 mole of C_2H_5OH. When the sodium and the potassium salts were prepared by the author in the higher alcohols by their treatment with the metal, and proper equilibrium was established with the traces of water, the above salts free from alcohol of crystallization were always obtained.

Oddo and Vassallo[5] obtained the red monopotassium salt from (absolute) alcohol. Bassett and Halton claim to have disproved the formation of the red salt, because they obtained the white salt of Kober when they used (ordinary) alcohol. These apparent contradictions can be understood because the experiments of this paper point out the modifying influence of traces of water in various solvents.

[7] Cornog, THIS JOURNAL, **43**, 2573 (1921).

[8] Kuster, *Z. anal. Chem.*, **41**, 474 (1904).

dicated as $HOCaCOOCC_6H_4C(C_6H_4OH)=C_6H_4=O\cdot 2H_2O$, and whose anhydrous salt, as $O(CaOOCC_6H_4C(C_6H_4OH)=C_6H_4=O)_2$.

The first formula involves the elimination of the phenol hydroxyl, an assumption which is disproved by the evolution of phenol itself at high temperatures. Furthermore, the analyses confirm the latter formulas:

Calcd. for $C_{20}H_{12}O_4Ca\cdot 2^1/_2H_2O$	Ca, 9.98; $2.5H_2O$, 11.22
Calcd. for $2(C_{20}H_{14}O_5Ca\cdot 2H_2O)$	Ca, 9.77; $5H_2O$, 10.98
Calcd. for $C_{20}H_{12}O_4Ca$	Ca, 11.25
Calcd. for $C_{40}H_{26}O_9Ca_2$	Ca, 10.97
Found by M and P in the hydrated salt	Ca, 10.1; water, 11.3
Found by M and P in the anhydrous salt	Ca, 11.5; and 11.6
Found by the author in the hydrated salt	Ca, 9.61
Found by the author in the anhydrous salt	Ca, 10.74

White Calcium Salt.—Equivalent quantities of freshly ignited marble and phenolphthalein were placed in ordinary 95% alcohol. At first a very red solution and a red solid were formed. After shaking often during days and weeks, the red solution became pink and the red solid was replaced by a fluffy, white solid. By shaking and letting stand for a few seconds, the solution with suspended white solid could be decanted from the heavier red solid, filtered, washed with alcohol, dried and analyzed.

Anal. Calcd. for $C_{20}H_{16}O_6Ca\cdot 2H_2O$: H_2O, 14.72. Found: H_2O, 14.50. Calcd. for $C_{40}H_{26}O_9Ca_2$ (see above): Ca, 10.97. Found: Ca, 10.96.

When dehydrated, this white salt became deep red at 110° and brown-black at 150°; both forms became bright red in moist air. Because the green anhydrous salt of Meyer and Posner becomes red on standing in the air and green again on heating, apparently the two anhydrous salts are two different compounds. However, when the green salt is pulverized in the absence of moisture, it becomes red, hence the green color is merely a fluorescent property of large red crystals.

Piperidine Phenolphthalein.—Upon mixing equivalent quantities of piperidine and phenolphthalein in methyl ethyl ketone or in alcohol, heating was observed; on cooling, white needles were obtained. After filtering and drying, they were found to give off slowly the odor of piperidine. On heating to 110° or higher, the material remained white.

Anal. Calcd. for $C_{20}H_{14}O_4\cdot C_5H_{11}N$: loss in weight, 21.10. Found: 20.95.

Because this additive compound contains no carbinol hydroxyl, it gives no color on being heated. With water it yields a red solution because of preliminary hydration, followed by dehydration.

Formula PP = $C_{20}H_{14}O_4$	Method used	Color hydrated salt	Color anhydrous salt	Crystal form (hydrated)	Calcd. H_2O	Found H_2O	Calcd. M	Found M
$2PP\cdot Ba(OH)_2\cdot 4H_2O$	b	White (violet)	Red	Needles	10.24	10.66	15.61	15.30
$2PP\cdot S(OH)_2\cdot 4H_2O$	b	White (pink)	Red	Needles	10.85	11.48	10.55	10.24
$2PP\cdot Cu(OH)_2\cdot 3H_2O$	d	Grass-green	Brown-black	Needles	9.13	9.32	8.07	8.10
$2PP\cdot Co(OH)_2\cdot 3H_2O$	c	White (red)	Brown-black	Needles	9.20	9.48	7.53	7.74
$2PP\cdot Mn(OH)_2\cdot 3H_2O$	c	White (brown)	Black	Needles	9.25	9.66	7.05	7.39
$2PP\cdot Cd(OH)_2\cdot 3H_2O$	d	White	Red	Needles	8.61	8.91	13.43	13.65
$2PP\cdot Zn(OH)_2\cdot 3H_2O$	d	White	Scarlet	Needles	9.12	9.66	8.28	8.30

Summary

1. A number of new salts of phenolphthalein have been prepared and studied. They are always additive compounds of phenolphthalein and the base. Usually two or more molecules of crystal water are also present.

2. It has been demonstrated that most hydrated salts are colorless and become colored by loss of water. Loss of water can be effected by heat, pressure, friction or certain solvents and such loss of water is probably a dehydration from the carbinol form to the quinoid form. The colors of dehydrated salts, containing either chromogenic or non-chromogenic metals, differ widely.

3. The probable cause of color of phenolphthalein salts is the quinoid chromophore. Hydration and dehydration are important influences effecting changes in color. Isomerization, neutralization, addition, hydrolysis and ionization attend phenolphthalein phenomena, but precede or are incidental to the transforming of colorless carbinol forms to the colored quinoid form.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

THE PREPARATION AND PROPERTIES OF SOME SUBSTITUTED 2-METHYLTHIOPHENES

BY ALVIN F. SHEPARD

RECEIVED MARCH 14, 1932 PUBLISHED JULY 6, 1932

In order to identify certain thiophene homologs in pyrolysis products, 2-methyl-5-ethylthiophene, 2-methyl-4-ethylthiophene and 2,3-dimethylthiophene were prepared for comparison. The preparation and properties of these compounds are reported here since these thiophene homologs were either unknown or imperfectly described.

2-Methyl-5-ethylthiophene was obtained in 40% yield by a modified Wolff reduction which consisted of heating the semicarbazide of 2-methyl-5-acetothienone with moist powdered potassium hydroxide. Steinkopf[1] has prepared this substituted thiophene in 10% yield by a Clemmensen reduction of 2-methyl-5-acetothienone, but he obtained insufficient material for determination of its physical properties.

The other two thiophene homologs were synthesized by the action of phosphorus sulfides on the proper substituted levulinic acids. While 2,3-dimethylthiophene has been prepared by Paal and Püschel[2] and by Grünewald,[3] it is noteworthy that our specimen had a boiling point about 3° higher than reported by them. This observation was checked on a purer

[1] W. Steinkopf, *Ann.*, **424**, 22 (1923).

[2] Paal and Püschel, *Ber.*, **20**, 2559 (1887).

[3] Grünewald, *ibid.*, **20**, 2586 (1887).

preparation obtained from 5-chloromercuri-2,3-dimethylthiophene. Table I summarizes the most significant data regarding these compounds.

TABLE I

SUBSTITUTED THIOPHENES

	2-Methyl-5-ethyl-	2-Methyl-4-ethyl-	2,3-Dimethyl- (a) From the mercurichloride	(b) from β-methyl-levulinic acid
Corr. boiling range, 760 mm.	159.8–160.4°	162–164°	140.2–141.2°	140.2–142.2°
F. p. range	−68.4 to −68.6°	−59 to −60°	−48.9 to −49.1°	
d_4^{20}	0.9663	0.9742	1.0021	1.0016
d_4^{30}	0.9577	0.9650	0.9919	
n_D^{20}	1.5073	1.5098	1.5192	1.5194
n_D^{30}	1.5024	1.5048	1.5140	
% S calcd.	25.42	25.42		28.59
% S found	25.47, 25.42	25.25, 25.34		28.44, 28.37
Mol. wt. calcd.	126	126		
Mol. wt. found	126, 125	127, 126		
M. R. calcd.	39.4	39.4	34.7	34.7
M. R. obs.	38.9, 38.9	38.7, 38.8	34.0, 34.0	34.0
Indophenin reaction	Red-brown	Green	Green	Green

The freezing points were measured with a toluene thermometer and are reliable to ±1°. Molecular weights were determined cryoscopically in benzene. The indophenin tests were made by adding a drop of the substituted thiophene to a solution of isatin in sulfuric acid containing a trace of nitric acid, and the color reported is the one which developed after the mixtures had stood for five to fifteen minutes.

Experimental Part

2-Methyl-5-ethylthiophene.—2-Methyl-5-acetothienone semicarbazide was prepared by the method of Steinkopf. It melted at 224.5° (with decompn.); Steinkopf gives 225°. Fifty grams of the finely powdered potassium hydroxide and 35 g. of the semicarbazide were placed in a 500-cc. distilling flask, 5 cc. of water was added and the whole mass was thoroughly mixed. The flask was then heated with a free flame as long as liquid distilled over. The product from three runs was combined, steam distilled once to separate a small amount of yellow solid which accompanied the methylethylthiophene, dried and fractionated over sodium. The yield of pure material having the constants indicated in the table was 40%. This thiophene homolog has a very characteristic and pleasant odor, similar to that of *p*-ethyltoluene.

2-Methyl-4-ethylthiophene.—α-Ethyllevulinic acid was obtained by the procedure of Fittig and Young,[4] and boiled from 161–166° (uncorr.) at 20 mm. Its semicarbazone had m. p. 171–172° with slight gas evolution; Gault and Solomon[5] give 171–172°. The acid was converted to the sodium salt, which was dried over phosphorus pentoxide at 100°. The sodium salt was powdered, thoroughly mixed with twice its weight of sand, and the mixture was distilled from a retort heated with a free flame. The resulting distillate was washed with cold sodium hydroxide solution and fractionated over

[4] Fittig and Young, *Ann.*, **216**, 39 (1883).

[5] Gault and Solomon, *Ann. chim.*, [10] **2**, 205 (1924).

sodium, which separated a small amount of material boiling below 140°. The purified 2-methyl-4-ethylthiophene was obtained in 20% yield (based on ethyllevulinic acid).

2,3-Dimethylthiophene.—β-Methyllevulinic acid was obtained by the excellent method of Pauly, Gilmour and Will,[6] and boiled from 130–132° (uncorr.) at 10 mm. On heating 30-g. portions of this acid with 35-g. portions of powdered phosphorus pentasulfide, a vigorous reaction took place and the product was distilled out as soon as the reaction slowed down. The crude product was worked up as before. The purified 2,3-dimethylthiophene was obtained in 20% yield.

As a check on the high boiling point observed, a specimen of 5-chloromercuri-2,3-dimethylthiophene was purified by crystallization until it melted with slight decomposition at 218.5–219.5 (corr.). Steinkopf[7] gives the melting point of this compound as 213–214° (with decomposition). The 2,3-dimethylthiophene was recovered quantitatively from this mercury compound by heating with hydrochloric acid, and the specimen thus obtained boiled entirely in the range 140.2–141.2° (corr.). The constants of both specimens are given in the table.

Summary

The preparation and physical properties of 2,3-dimethylthiophene, 2-methyl-4-ethylthiophene and 2,5-methylethylthiophene are presented.

[6] Pauly, Gilmour and Will, *Ann.*, **403**, 145 (1914).

[7] Steinkopf, *ibid.*, **424**, 46 (1923).

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. IX. THE PRODUCTS OF DESTRUCTIVE DISTILLATION OF EBONITE

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND ALVIN F. SHEPARD

RECEIVED MARCH 14, 1932 PUBLISHED JULY 6, 1932

Introduction

It has been shown that there is a definite relationship[1] between the rubber molecule and its pyrolysis products, and consequently the thermal decomposition of ebonite has been undertaken to throw light on the nature of the rubber sulfur complex.

It was relatively simple to correlate the pyrolysis products of raw rubber with the formula of the parent molecule, as the rubber formula had been previously established by oxidation. However, the formula of ebonite is still unknown, and cannot be arrived at by ordinary methods, because ebonite is amorphous, insoluble, non-volatile, completely saturated, and inert toward chemical agents. A correlation of its pyrolysis products may thus be the only way of establishing its formula.

The pyrolysis products of ebonite, the decomposition products of a mixture of rubber and sulfur, and the interaction of sulfur and the pyrolysis

[1] Midgley and Henne, THIS JOURNAL, **51**, 1215 (1931).

products of raw rubber have been investigated to establish a basis from which the formula of ebonite may be derived.

The present paper presents the study of the products obtained when ebonite is destructively distilled.

Procedure.—Thirty-six kilograms of ebonite were destructively distilled in the manner reported previously. The volatile products were progressively condensed by means of warm water ice water and solid carbon dioxide. The non-condensed gases were washed through a copper sulfate solution to eliminate hydrogen sulfide, and finally led through another condenser cooled with carbon dioxide. The condensed products were subjected to fractional distillation, and from the various cuts thus obtained the thiophene homologs were separated by mercuration.

Results.—The amount of hydrogen sulfide liberated during pyrolysis accounted for approximately one-half of the sulfur originally present in the ebonite. As a consequence, the oils obtained were of a highly unsaturated character. An examination of the oils boiling below 170° established the presence of mercaptans, sulfides, thiophene homologs and *m*-xylene. The examination failed to detect disulfides. The oils boiling above 170° were rich in sulfur; they were not further investigated. The limited stability of a portion of the sulfur compounds precluded their separation, and hence the determination of their constitution. The thiophenes and the hydrocarbons were stable enough to be successfully investigated, and it was thus possible to isolate and identify 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. At the same time it was shown that benzene, toluene, thiophene, 2,5-dimethylthiophene, 2,3-methylethylthiophene or trimethylthiophenes were not present in significant quantities. Similarly, the absence of other isomers of the thiophene homologs was established. The yields were: thiophenes, 1%; xylene, 0.1%, of the total quantity of ebonite used.

Experimental Part

The ebonite used in this investigation was prepared by the Inland Manufacturing Company of Dayton, Ohio, through the kindness of Dr. A. H. Flower, to whom we here wish to express our thanks. The following mix was used: first latex crepe, 100, sulfur, 32, diphenylguanidine, 2, "Kadox," 2, stearic acid, 2. The mix was cured for eight hours at 148°; analysis showed 0.1% free sulfur at the end of this time.[2]

[2] The effect of the ingredients other than sulfur and rubber in the ebonite may be discounted, as shown by the following experiments. A small batch of ebonite, prepared from a crepe rubber–sulfur mix containing 32% sulfur and no accelerators, was destructively distilled. In the distillate, 2-methylthiophene, 2,3-dimethylthiophene and *m*-xylene were positively identified. Thiophene, benzene, toluene, 3-methylthiophene and *p*-ethyltoluene were absent, while 2,4-dimethylthiophene and 2-ethyl-5-methylthiophene appeared to be present, although they were not positively identified. An ebonite was also prepared from sodium–rubber containing 32% sulfur and no accelera-

Thirty-six kilograms of this ebonite were cracked as previously described. The vapors were progressively condensed at 100, 0 and −80°. The condensate obtained at −80° was chiefly hydrogen sulfide and quite free of hydrocarbons boiling below 30°. A rough estimate of the amount of hydrogen sulfide liberated was made by passing the cracked gases through copper sulfate solutions. Table I summarizes the results.

TABLE I

	Liquid	H_2S	Water	Coke	Uncondensed gases and loss
Yield on ebonite, %.....	59	13	4	6	18

The liquid was topped to 200°. The higher boiling materials contained 14.2% sulfur; they were not further investigated. The distillate below 200° (3600 g. or 10% of the original liquid) was systematically fractionated. After three runs, the material boiling below 120° was repeatedly washed with alkali to remove mercaptans completely, and the fractionation was resumed and carried out to its practical limit. Table II shows the results of the final fractionation together with the physical properties and sulfur content of the fractions. Double bond determinations were made only on the fractions containing little sulfur.

TABLE II

Temp., °C.	Volume, cc.	dV/dT	d_{15}^{20}	n_D^{20}	Δ	S, %
30–36	14	2	0.672	1.389	0.9	
36–40	8	2	.675	1.400	.9	
40–51	6	0.5		1.399	.8	1.1
51–57	12	2	.702	1.392	.6	2.1
57–61	22	5	.704	1.393	.7	1.7
61–65	13	3	.714	1.400	.7	1.1
65–69	26	7	.725	1.413	.9	1.3
69–73	22	5	.743	1.425	1.0	1.5
73–77	12	3	.770	1.436	0.9	2.2
77–80	12	4	.761	1.429	.8	1.9
80–88	17	2	.755	1.416	.6	1.7
88–90	15	8	.742	1.410	.7	1.0
90–94	21	5	.739	1.413	.8	0.6
94–96	18	9	.741	1.416		
96–105	22	2	.797	1.441		
105–107	23	12	.847	1.461		
107–109	54	27	.867	1.468		13.0
109–111	125	63	.873	1.471		14.5
111–113	55	28	.856	1.464		13.5
113–119	28	5	.835	1.454		9.1
119–125	30	5	.813	1.446		7.4
125–130	33	7	.843	1.457		11.4
130–134	40	10	.861	1.467		13.9
134–136	26	13	.873	1.472		14.0
136–138	111	56	.894	1.485		14.5
138–140	194	97	.909	1.490		15.4
140–142	39	20	.916	1.491		16.8

tors. The pyrolysis products of this sodium rubber ebonite were also quite similar to those from crepe rubber ebonite. The mercuration treatment allowed the recovery of small amounts of thiophene homologs, similar in their indophenin reactions to those obtained from the crepe rubber ebonite.

TABLE II (*Concluded*)

Temp., °C.	Volume, cc.	dV/dT	d_{15}^{20}	n_D^{20}	Δ	S, %
142–145	20	7	.905	1.488		16.2
145–151	15	3	.887	1.482		14.5
151–156	25	5	.884	1.480		14.6
156–159	55	18	.906	1.487		18.3
159–160	129	129	.920	1.494		
160.0–160.5	125	250	.929	1.497		
160.5–161.5	125	125	.935	1.500		19.6
161.5–162.7	100	83	.938	1.502		Composite
162.7–165.0	120	52	.936	1.504		sample
165–169	100	25	.935	1.505		17.1
169–172	100	33	.926	1.501		16.9
172–175	100	33	.919	1.497		17.3
175–180	100	20	.919	1.495		

Each of the three main fractions, b. p. 109–111°, 138–140° and 160–160.5°, was a complex mixture. Distillation from aniline separated these mixtures roughly into hydrocarbon-rich fractions and sulfur-rich fractions, but since this was insufficient, chemical methods were preferred.

Mercaptans and Disulfides.—A mercaptan concentrate was isolated by steam distilling the alkali washings of the ebonite fraction boiling below 120°. It weighed only 8 g. and boiled chiefly from 66–80°. It had the characteristic mercaptan odor and gave typical mercaptan reactions with iodine, alcoholic lead acetate, sodium plumbite and mercuric oxide. The ebonite fractions boiling from 100–180° contained mere traces of mercaptans.

Disulfides were absent from the ebonite fractions boiling below 170°; this was shown by the failure to form mercaptans on reduction with zinc and glacial acetic acid.[3]

Thiophenes and Aromatic Hydrocarbons.—Thiophene and its lower homologs are very readily mercurated.[4] Thiophene is quantitatively extracted from benzene[5] by a boiling solution of mercuric acetate in dilute acetic acid; it forms a di-mercuri compound, and is readily regenerated from this compound by boiling hydrochloric acid. The various ebonite fractions were refluxed for thirty minutes or more with Dimroth's reagent (40 g. mercuric oxide), 40 cc. glacial acetic acid and 200 cc. water) and subjected to steam distillation. This operation removed unreacted aromatic and saturated hydrocarbons and left behind a complex mixture, from which the thiophenes were regenerated in a fair state of purity by boiling hydrobromic acid. The mercuric acetate treatment always caused the loss of the olefins and of up to 70% of the sulfur compounds. In order to show that this loss of sulfur derivatives was not due to the preferential destruction of some definite thiophene homolog, the mercuration and regeneration of thiophene, 2-methylthiophene, and of 3-methylthiophene were checked. None was appreciably oxidized; all were completely regenerated from their mercury compounds by hydrobromic acid. This check was regarded as important because Volhard reports that 2,5-dichloromercuri-3-methylthiophene is very difficult to split with acids.

Other Sulfur Compounds.—Many unsuccessful attempts were made to isolate by

[3] Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, **19**, 1281 (1927).

[4] Volhard, *Ann.*, **267**, 172 (1892); Steinkopf and Bauermeister, *ibid.*, **403**, 50–72 (1914); (a) Steinkopf, *ibid.*, **413**, 310–333 (1917); (b) **424**, 23–61 (1921); (c) **428**, 138 (1922).

[5] Dimroth, *Ber.*, **32**, 759 (1899).

other methods the sulfur compounds lost in the mercuration procedure. Significant are the following observations.

Fractions containing these sulfur compounds react with mercurous nitrate monohydrate, a reagent used by Faragher, Morrell and Monroe[3] for the quantitative removal of sulfides from thiophene and hydrocarbons.

Diethyl sulfide may be recovered from its mixture with a hydrocarbon and thiophene by shaking with a solution of mercuric acetate and steam distilling the mercuric acetate solution but no sulfur compound is recoverable from the 109–113° cuts in this way.

The ebonite distillates did not react appreciably with dimethyl sulfate, a reagent which reacts with dimethyl sulfide on gentle warming.

The early experiments with aniline fractionation showed that in the case of the large fractions boiling at 107–113°, 136–142° and 159–165°, the sulfur compounds lost had physical properties not widely different from the thiophenes with which they were associated.

A proposed explanation is that the lost sulfur compounds represent members of an homologous series of dihydrothiophenes.

Tests for Individual Compounds.—The mercuration procedure was systematically applied to all the ebonite distillates boiling in the range 60–165°. Unless otherwise stated, all mercury derivatives were prepared and purified exactly according to the directions of Steinkopf.[4b]

Thiophene and Benzene.—One drop of oil was recovered from the mercury compounds obtained from the ebonite fractions boiling from 66–88°. This drop did not give the indophenin reaction; thiophene was therefore absent. The steam distillate from the mercury compounds was treated with bromine water and steam distilled; 1 cc. of an oil was obtained. Nitration to dinitrobenzene was attempted but none could be isolated.

2-Methylthiophene.—The product isolated boiled at 111.5–112.5° (741 mm.), and had d_4^{20} 1.017, n_4^{20} 1.5132, molecular refraction observed 29.0, theoretical 30.1. It gave the green indophenin reaction characteristic of 2-methylthiophene. The following derivatives were prepared: 5-chloromercuri-2-methylthiophene, m. p. 204°, alone and in a mixture with authentic material; 2-methylthiophene-5-mercurithiocyanate, m. p. 200–201° (decomp.); tribromo-2-methylthiophene, m. p. 83°. Steinkopf gives the melting points of the first two derivatives as 204° and 202–204° (decomp.), respectively. Gattermann, Kaiser and Meyer[6] give a melting point of 86° for tribromo-2-methylthiophene and state that a mixture of the 2- and the 3-isomers is inseparable by crystallization and melts at 74°. Comparison of the relative amounts of alcohol-insoluble material formed on mercurating the thiophene from ebonite and synthetic 3-methylthiophene indicated[7] that less than 10% of 3-methylthiophene could have been present in the ebonite product.

Toluene.—The steam distillate containing the toluene was brominated at 0° with bromine water and steam distilled to separate the unreacted constituents from olefin bromides. After washing with sulfuric acid the product boiled at 109.5–111.5° and had n_D^{20} 1.4812. A saturated compound was present with the toluene since the material was not completely soluble in 10% oleum. Nitration gave dinitrotoluene of m. p. 69–70° alone and in a mixture with authentic material. A check experiment showed that no significant amount of toluene could have been mercurated and thus lost in the procedure of separation.

---

[6] Gattermann, Kaiser and Meyer, *Ber.*, **18**, 3009 (1885).

[7] Later experiments have shown that 3-methylthiophene is readily formed by the interaction of isoprene and boiling sulfur.

Dimethylthiophenes.—The thioxene mixture as isolated boiled at 139.5–141.5° (745 mm.) corr. and had n_D^{20} 1.5137 and d_4^{20} 0.984. Mercuration with mercuric chloride according to Steinkopf's procedure yielded a product completely soluble in benzene or alcohol. This shows the absence of 3,4-dimethyl- or 3-ethylthiophene; Steinkopf states that these isomers form di-mercuri compounds insoluble in these or other low-boiling solvents. The boiling point of the mixture is too high to be compatible with the presence of any significant quantity of 2-ethylthiophene (b. p. 132–134° corr.).[8]

Fractional crystallization of the mercury chloride compounds of the ebonite thioxenes from benzene permitted the isolation of 50% of the mercury compounds as 5-chloromercuri-2,3-dimethylthiophene, m. p. 217.5–218.5° (decomp.) alone and in a mixture with authentic material. This substance was converted to 2,3-dimethylthiophene-5-mercurithiocyanate, which shrunk and blackened at about 198° and did not melt up to 240°. Steinkopf states that this compound darkens at 200–202° and does not melt below 240°. Further confirmation of the presence of 2,3-dimethylthiophene was obtained by permanganate oxidation of the original thioxene mixture. A mixture of mono- and dicarboxylic acids resulted and the mono acid was steam distilled out from a very concentrated solution. Recrystallized twice from water it melted at 140–141° and its melting point was raised by mixture with the acid of m. p. 143° obtained similarly from the oxidation of synthetic 2,3-dimethylthiophene. The dicarboxylic acids gave the fluorescein reaction strongly.

Anal. of monocarboxylic acid: (a) from synthetic 2,3-dimethylthiophene; C, 50.8, 50.9; H, 4.1, 4.2. Calcd. for $C_6H_6O_2S$: C, 50.7; H, 4.3. (b) From ebonite thioxene: molecular weight by alkali titration, 141.5; calcd. for $C_6H_6O_2S$, 142.

The other mercury compounds occurring with 5-chloromercuri-2,3-dimethylthiophene were much more soluble in all solvents, melted mostly at 135–150°, and could not be purified satisfactorily by crystallization. Steinkopf has noted a considerable difference in the rates at which the substituted thiophenes mercurate, and a separation of 2,4-dimethylthiophene derivatives was accomplished by the application of this principle. The above-mentioned mixture of mercury compounds was converted to the thioxenes with hydrogen bromide and the thioxenes were remercurated. After five minutes the mercury compound formed was separated from the mercuration mixture and reconverted to the thioxenes. The mercuration was then repeated, and after two minutes the formed mercury compound was again removed. The final amount of this mercury compound corresponded to 10% of the original mixture of mercury compounds obtained from the ebonite thioxenes. Crystallized from benzene, it melted at 168–169° in a bath preheated to 165°; on slower heating it sintered together somewhat above 170° but did not melt. The mercuric chloride addition product of oxodihydromercuri-2,3-dimethylthiophene is stated by Steinkopf to melt at 167–168° on rapid heating; slow heating causes only a gradual sintering together. From this compound were prepared 5-chloromercuri-2,4-dimethylthiophene, m. p. 137.5–138.5°; 2,4-dimethylthiophene-mercurithiocyanate, m. p. 175–177° (sinters at 173°); and 5,5′-mercuri-bis-2,4-dimethylthiophene, m. p. 160–161° (with sintering). Steinkopf gives the melting points of these substances as 138–139°, 173–175° (sinters at 171°) and 160–161° (with sintering), respectively. The presence of 2,4-dimethylthiophene in the ebonite distillates is thus proved.

An attempt was made to isolate 2,5-dimethylthiophene by a similar method based on the principle that the compound mercurates much more slowly than the 2,3- and 2,4-isomers. None was found.

***m*-Xylene.**—The xylene fraction was separated from olefins in the same way as the toluene. The product had b. p. 138–139° (746 mm.) (corr.), d_4^{20} 0.852 and n_D^{20} 1.4895. Sulfonation with oleum left about 10% of saturated hydrocarbon. According to

[8] Meyer and Kreis, *Ber.*, **17**, 1560 (1884).

Timmermans[9] *m*-xylene has b. p. 139.3° (760 mm.) and d_4^{20} 0.8641. Ten drops of the xylene fraction was added to 10 cc. of concentrated sulfuric acid and 5 cc. of fuming nitric acid; the mixture was boiled for two minutes, then poured on ice and diluted with water. The precipitate was filtered off, washed with water and then with 15 cc. of cold 50% alcohol. The dried product showed m. p. 177–179°; after one crystallization from 50% alcohol it melted at 181–182° alone and in a mixture with authentic material. This proves the presence of *m*-xylene, substantially free of isomers.

2-Methyl-5-ethylthiophene.—The product first recovered from the mercuration procedure still contained unsaturated compounds and had d_4^{20} 0.957. To eliminate the unsaturated material the procedure of mercuration and regeneration was repeated. The product thus obtained boiled at 159.8–161.3° (chiefly 160.1–160.6°), had a freezing point −74.2°, d_4^{20} 0.958, n_D^{20} 1.5048 and a mol. wt., as determined by the freezing point depression in benzene, of 124.2, 126.5.

Anal. Calcd. for $C_7H_{10}S$: S, 25.42. Found: S, 24.05, 24.10, 23.90.

A specimen was prepared from the mercury acetate compound crystallized from glacial acetic acid; this preparation boiled at 159.5–160.6°, had a freezing point of −69.4°, d_4^{20} 0.9644, n_D^{20} 1.5063, and contained 25.28, 25.31% S. Presumably the earlier preparation still contained a small amount of hydrocarbon.

Synthetic 2-methyl-5-ethylthiophene boils at 159.8–160.4° and has[10] the freezing point −68.4°, d_4^{20} 0.9663 and n_D^{20} 1.5073. The freezing point of the product from ebonite (f. p. −74.2°) was raised by admixture with the synthetic material. It is noteworthy that this 2,5-disubstituted thiophene mercurates more slowly than the other compounds heretofore described, a behavior which parallels that reported by Steinkopf for 2,5-dimethylthiophene. Both synthetic 2-methyl-5-ethylthiophene and the product from ebonite (f. p. −74.2°) gave an intense red-brown color when added to a solution of isatin in commercial sulfuric acid. Dr. W. R. Brode has very kindly compared the absorption spectra of both these colorations with a spectrophotometer, and has found no difference whatever in the spectra.

It is evident that the material from ebonite is 2-methyl-5-ethylthiophene, reasonably free from isomers.

A trimethylthiophene, especially the 2,3,5-isomer, might be expected to mercurate with extreme difficulty, and these compounds were sought in the steam distillate from the mercuration. Youtz and Perkins[11] state that 2,3,5-trimethylthiophene dissolves in sulfuric acid and is reprecipitated apparently unchanged on dilution. Schulze[12] has recovered thiophene and its homologs by diluting with water and steam distilling the sulfuric acid washings of various aromatic hydrocarbons obtained from coal tar. Accordingly, the steam distillate from the mercuration of the ebonite fractions boiling in the neighborhood of 160° was carefully washed, cold, with 2 volumes of concd. sulfuric acid. The sulfuric acid extract was drawn off and ice and water were added to it, which caused the separation of an oil. The oil was removed, steam distilled, and then distilled over sodium. There was thus recovered 2 g. of a product of b. p. 158–168° which had n_D^{30} 1.484. A measurement of the depressions of the freezing point of 2-methyl-2-ethylthiophene caused by the addition of this material and of *n*-nonane was made. This measurement showed that at least 50% of the material recovered by sulfuric acid treatment was 2-methyl-5-ethylthiophene, which fact, in view of the low refractive index of the material, shows the practical absence of trimethylthiophenes.

[9] Timmermans, *J. chim. phys.*, **27**, 2 (1930).

[10] The preparation and physical properties of the synthetic specimen are described in a separate paper now submitted for publication in THIS JOURNAL.

[11] Youtz and Perkins, THIS JOURNAL, **51**, 3511–3516 (1929).

[12] Schulze, *Ber.*, **18**, 497 (1885).

Aromatic hydrocarbons were present only in insignificant amount in the ebonite fractions boiling from 156–165°, since less than 1 g. of hydrocarbon (b. p. 160–163°, n_D^{30} 1.472) was recovered from the sulfuric acid washing of the steam distillates.

TABLE III

AMOUNTS OF PRODUCTS RECOVERED BY PYROLYSIS OF 36,000 G. OF EBONITE

Compound	Recovered, g.	Compound	Recovered, g.
Benzene	<0.5	2,4-Dimethylthiophene	10
2-Methylthiophene	10	*m*-Xylene	50
Toluene	1	Aromatic hydrocarbon, b. p. *ca.* 160°	<1
2,3-Dimethylthiophene	50	2-Methyl-5-ethylthiophene	240

Summary

The following compounds have been identified in the products obtained from ebonite by destructive distillation: 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. These results will be used to derive the structural formula of ebonite.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF BENZOYLACETIC ESTER AND SOME OF ITS HOMOLOGS

BY JOHN B. DORSCH AND S. M. MCELVAIN

RECEIVED MARCH 14, 1932 PUBLISHED JULY 6, 1932

Although benzoylacetic ester was first prepared by Baeyer[1] by the hydration of phenylpropiolic ester, this method has certain disadvantages that reduce its preparative value.[2] The most satisfactory methods that may be found in the literature are two developed by Claisen. One of these involves the direct condensation of ethyl benzoate with ethyl acetate in the presence of sodium ethoxide,[3] and although a 33% yield of product is claimed, the actual weight of benzoylacetic ester reported as having been obtained shows the yield to be only 26% of the theoretical. In the other method benzoylacetic ester is obtained by the partial hydrolysis of benzoylacetoacetic ester.[4] Recently, failures to duplicate the yield claimed in Claisen's first method and modifications of the second method have been reported by Shriner and Schmidt.[5]

A number of the homologs of benzoylacetic ester have been prepared

[1] Baeyer, *Ber.*, **15**, 2705 (1882).

[2] Hope and Perkin, *J. Chem. Soc.*, **95**, 2047 (1909).

[3] Claisen and Lowman, *Ber.*, **20**, 653 (1887).

[4] Claisen, *Ann.*, **291**, 67 (1896).

[5] Shriner and Schmidt, THIS JOURNAL, **51**, 3636 (1929).

by Perkin and co-workers[6] by the alkylation of this ester with an alkyl iodide in alcoholic solution in presence of sodium ethoxide. Although no yields are reported the idea is conveyed that the procedure is quite satisfactory. Experiences with the alkylation of benzoylacetic ester in this Laboratory by Perkin's method as well as with one using metallic sodium in the absence of alcohol[7] have been far from gratifying. Besides being obtained in quite low yields, the product was a mixture of the alkylated and unalkylated benzoylacetic esters.

This paper reports the results of a study of the preparation of benzoylacetic ester and its homologs, ethyl α-benzoylpropionate, ethyl α-benzoylbutyrate and ethyl α-benzoylvalerate. These esters were prepared by the hydrolysis of the imino ether hydrochlorides derived from the corresponding α-benzoyl alkyl cyanides. These latter compounds were obtained by the condensation of ethyl benzoate with the alkyl cyanide by means of sodium ethoxide. The steps in the preparation may be illustrated thus

$$C_6H_5COOC_2H_5 + RCH_2CN \xrightarrow{NaOC_2H_5} C_6H_5COCH(R)CN \xrightarrow[HCl]{C_2H_5OH}$$

$$C_6H_5COCH(R)C(OC_2H_5)=NHHCl \xrightarrow{H_2O} C_6H_5COCH(R)COOC_2H_5$$

The yields of the benzoyl alkyl cyanides varied from 53–60%, while the yields of the esters from the cyanides were 64–74%. The over-all yields of each of the keto esters from ethyl benzoate was 35–44% of the theoretical.

An interesting variation in the behavior of the benzoyl alkyl cyanides was noted in their conversion into the esters. When the intermediate imino ether hydrochlorides were treated with alcohol containing the theoretical amount of water for their hydrolysis, benzoylacetic ester was obtained from benzoyl methyl cyanide with no side product, but from α-benzoyl ethyl cyanide a considerable amount of benzoyl propionamide was isolated along with the keto ester. From α-benzoyl propyl cyanide and α-benzoyl butyl cyanide practically the entire yield in each case was the corresponding amide. This amide formation could be considerably reduced, but not completely prevented, if about three times the required amount of water, containing a small amount of hydrochloric acid, was used for the hydrolysis.

A study also was made of the direct condensation of ethyl benzoate with ethyl acetate and certain of its homologs in the presence of sodium ethoxide. Not only was it possible in the case of benzoylacetic ester to duplicate the yields reported by Claisen and Lowman,[3] but by certain modifications the yield was raised to 37% of theory. With such a yield the direct condensa-

[6] Perkin and co-workers, *J. Chem. Soc.*, **45**, 179 (1884); **49**, 160 (1886); **95**, 2047 (1909).

[7] *Cf.* Folkers and Adkins, THIS JOURNAL, **53**, 1416 (1931).

tion procedure is to be preferred over the method involving the intermediate benzoyl methyl cyanide. The yields of the higher homologs by direct condensation were, however, much lower, being in the cases of ethyl α-benzoylpropionate and ethyl α-benzoylbutyrate 19 and 4%, respectively. The procedure through the α-benzoyl cyanides seems to be the most satisfactory method of preparation of these higher homologs not only because of the yield but on account of the high purity of the product which it affords due to the fact that the unalkylated and dialkylated products are necessarily absent.

Experimental

Materials Used.—The esters and cyanides which were used were dried over and distilled from phosphorus pentoxide. Sodium ethoxide was prepared by two previously described procedures.[8]

α-Benzoylalkyl Cyanides.—In a 3-necked 1-liter flask fitted with a mercury-seal stirrer, a long-stem dropping funnel and a reflux condenser were placed 150 g. (1 mole) of ethyl benzoate and 68 g. (1 mole) of sodium ethoxide. The mixture was warmed by an oil-bath to about 80° and stirred until it became a homogeneous gelatinous mass. Then 1.25 moles of the alkyl cyanide was added slowly under the surface of this mass from the dropping funnel over a period of two hours. The temperature of the oil-bath was then raised to and maintained at 110–120°, in the case of methyl and ethyl cyanide, for ten hours with continuous stirring. When propyl and butyl cyanides were used it was found advantageous at this point to replace the reflux condenser with a short (18-cm.) Vigreux column, raise the temperature of the oil-bath to 140–160° and to allow the alcohol formed in the condensation to distil out slowly from the reaction mixture.

The reaction mixture was then cooled to about 0° in an ice-bath, treated with 400 cc. of ice water and 100 cc. of ether and shaken until the solid material had dissolved. The aqueous layer was then separated from the ether layer and acidified with dilute sulfuric acid. The precipitated benzoyl alkyl cyanide together with a small amount of benzoic acid was taken up in ether and the resulting ethereal solution washed with a saturated sodium bicarbonate solution to remove the benzoic acid. After drying over anhydrous sodium sulfate, the ether was removed by distillation. Benzoyl methyl

TABLE I

α-BENZOYLALKYL CYANIDES

Alkyl group	M. p., °C.	B. p., °C.	Yield, %	Analyses, N, % Calcd.	Found
Methyl[a]	80–81		56	..	..
Ethyl[b]		128–130 (3 mm.)	53	8.81	8.79
Propyl[c]		134–135 (3 mm.)	60	8.09	8.24
Butyl[c]		139–140 (3 mm.)	59	7.48	7.47

[a] Haller, *Compt. rend.*, **104**, 1448 (1887), reports this compound as melting at 80.5°. [b] Walther and Schickler, *J. prakt. Chem.*, [2] **55**, 306 (1897), obtained by the above procedure a small amount of α-benzoyl ethyl cyanide which they isolated as the phenylhydrazone, m. p. 100–104°. They could not obtain any satisfactory results with the higher cyanides. Meyer, *J. prakt. Chem.*, **147**, 190 (1889), reports this compound as a liquid but gives no physical constants. [c] These compounds do not appear to have been described previously in the literature.

[8] McElvain, THIS JOURNAL, **51**, 3128 (1929); Houben-Weyl, Vol. II, 1922, p. 578.

cyanide is a solid and was purified by recrystallization from naphtha (b. p. 90–125°). The higher homologs are liquids and were purified by distillation under diminished pressure.

α-Benzoyl Esters and Amides.—A solution of 50 g. of the benzoyl alkyl cyanide in 250 cc. of absolute alcohol was cooled to 0° and saturated with dry hydrogen chloride. After standing at room temperature for about twelve hours, the excess alcohol and hydrogen chloride were removed under diminished pressure. Then 100 cc. of absolute alcohol containing three times the theoretical quantity of water necessary for the hydrolysis of the imino ether hydrochloride and 3 cc. of concentrated hydrochloric acid were added to the residue and the resultant solution heated for thirty minutes on a steam-bath. The solution was then cooled and poured into 800 cc. of cold water. The ester layer which separated was taken up in ether and separated from the water layer. In certain cases a small amount of the solid amide remained insoluble in both the ether and water layers and was removed by filtration. The ether extract of the α-benzoyl esters was dried over sodium sulfate and after removal of the ether the ester was distilled under diminished pressure. It is advisable to use as low pressures as possible for these distillations in order to minimize the formation of the dehydro compounds. The boiling points and yields of these esters are summarized in Table II.

If only the theoretical quantity of water were employed for the hydrolysis of the imino ether hydrochlorides instead of three times the required amount as described above, the yield of benzoylacetic ester was unaffected but the yields of the higher homologs were considerably reduced. In each of these latter cases a sufficient amount of the corresponding amide was obtained to compensate for the reduction in the yield of the ester. These amides, which are summarized in Table II, were characterized by hydrolysis into the phenyl alkyl ketones.

TABLE II

α-BENZOYL ESTERS AND AMIDES

$C_6H_5COCH(R)COOC_2H_5$, R is	B. p., °C.	Yield, %, from cyanide	$C_6H_5COCH(R)CONH_2$, R is	M. p., °C.	Nitrogen analyses, % Calcd.	Found
H[a]	118–120 (1 mm.)	72	...	.....	...	...
CH_3[b]	128–130 (1 mm.)	64	CH_3[c]	145–146	7.91	7.83
C_2H_5[b]	134–135 (3 mm.)	74	C_2H_5[c]	148–149	7.33	7.22
$C_3H_7(n)$[b]	138–140 (3 mm.)	64	C_3H_7[c]	157–158	6.83	7.02

[a] Haller, *Bull. soc. chim.*, [2] **48**, 23 (1887), reports the preparation of benzoylacetic ester from benzoyl methyl cyanide. [b] *Cf.* Hope and Perkin, *J. Chem. Soc.*, **45**, 179 (1884); **47**, 241 (1885); **49**, 156–160 (1886); **95**, 2045 (1909). [c] Not previously described in the literature.

Direct Condensation of Ethyl Benzoate with Ethyl Acetate and its Homologs.—A mixture of 136 g. (2 moles) of sodium ethoxide and 300 g. (2 moles) of ethyl benzoate was placed in a 1-liter 3-necked flask fitted with a mercury-seal stirrer, a dropping funnel extending below the surface of the liquid, and a reflux condenser carrying a calcium chloride tube in the upper end. This mixture was stirred and heated in an oil-bath to 70–80° until the mass became a fairly homogeneous paste. Then 176 g. (2 moles) of ethyl acetate was added slowly from the dropping funnel over a period of about two

hours. The temperature of the oil-bath was then raised to 90° and the reaction mixture held at this temperature with continuous stirring for another two hours.[9]

The reaction mixture was then cooled and treated with a cold solution of 150 cc. of glacial acetic acid in 300 cc. of water and the ester layer taken up in ether. The ether extract was washed free of acid with sodium bicarbonate and, after removal of the ether, fractionated under diminished pressure. The yield of ester boiling over a 5° range amounted to 144 g. (37% of calcd.).

When the above procedure was followed using equivalent quantities of ethyl propionate and ethyl butyrate instead of ethyl acetate the yields of the corresponding keto-esters dropped to about 19 and 4% of the theoretical, respectively.

Summary

A method of preparation of a number of α-benzoyl alkyl cyanides and their conversion into the corresponding α-benzoyl substituted esters are described. The properties of the amides corresponding to certain of these esters are recorded.

A satisfactory method for the preparation of benzoylacetic ester by the direct condensation of ethyl benzoate with ethyl acetate is given.

[9] Claisen and Lowman[3] recommend mixing the reactants and heating for fifteen hours. It was found in the present work that this longer period of heating was not only unnecessary but somewhat disadvantageous since invariably 5–10% lower yields were obtained when this procedure was employed.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

ESTERS OF ORTHOFORMIC ACID

BY PETER P. T. SAH AND TSU SHENG MA

RECEIVED MARCH 14, 1932 PUBLISHED JULY 6, 1932

The discovery of the first orthoformic ester was connected with the famous Williamson synthesis.[1] The product from sodium ethoxide and chloroform was really an ether with three ethoxy groups attached to the same carbon atom. The reaction was further studied by a number of investigators,[2] notably Deutsch,[3] who synthesized five members of the homologous series (methyl, ethyl, *n*-propyl, *i*-butyl and *i*-amyl) and determined roughly their boiling points and densities. Pinner,[4] allowing various alcohols to react on form-imino-ether-hydrochlorides, succeeded not only in confirming Deutsch's work but also isolating a number of mixed ortho-

[1] Williamson and Kay, *Ann.*, **92**, 346 (1854).

[2] (a) Sawitsch, "Jahresbericht über die Fortschritte der Chemie," 391 (1860); (b) Bassett, *Ann.*, **132**, 54 (1864); (c) Ladenburg and Wichelhaus, *ibid.*, **152**, 164 (1869); (d) Stapff, *Z. Chem.*, 186 (1871); (e) Arnold, *Ann.*, **240**, 193 (1887); (f) Kaufmann and Dreger, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 55.

[3] Deutsch, *Ber.*, **12**, 115–119 (1879).

[4] Pinner, *ibid.*, **16**, 1643–1647 (1883).

formates. Of these, little was known regarding their physical properties except their boiling points.

By allowing metallic sodium to react with a mixture of chloroform and various alcohols, we have prepared seven tri-alkyl orthoformates in a very pure condition and determined carefully their simple physical constants.

Experimental

Preparation of Tri-alkyl Orthoformates.—Into a one-liter round-bottomed flask, with a reflux condenser, containing 150 g. of dry chloroform and 500 cc. of absolute alcohol (methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl and *i*-amyl), 69 g. of metallic sodium cut into sticks was introduced gradually in the course of two hours. For methyl and ethyl derivatives, the reactants were well cooled in ice water. The higher homologs showed retardation of reaction and initial heating was necessary. When the reaction was over, the flask was allowed to cool at room temperature for four hours. The

TABLE I

SIMPLE PHYSICAL CONSTANTS OF TRI-ALKYL ORTHOFORMATES

Tri-alkyl	Formula	B. p., °C.	d_4^{20}	d_4^{25}	n_D^{20}	n_D^{25}	From literature[2] B. p., °C.	d^{23}
Methyl	$C_4H_{10}O_3$	103–105	0.9676	0.9623	1.3793	1.3773	101–102	0.974
Ethyl	$C_7H_{16}O_3$	145–147	.8909	.8858	1.3922	1.3900	145–147	$.897_4^{18.8}$
i-Propyl	$C_{10}H_{22}O_3$	166–168	.8621	.8600	1.4000	1.3980	New compound	
n-Propyl	$C_{10}H_{22}O_3$	196–198	.8805	.8783	1.4072	1.4052	196–198	.879
i-Butyl	$C_{13}H_{28}O_3$	224–226	.8582	.8550	1.4120	1.4100	220–222	.861
n-Butyl	$C_{13}H_{28}O_3$	245–247	.8693	.8687	1.4180	1.4160	New compound	
i-Amyl	$C_{16}H_{34}O_3$	267–269	.8628	.8578	1.4233	1.4217	265–267	.864

TABLE II

MOLECULAR REFRACTIONS OF TRI-ALKYL ORTHOFORMATES

Structures	Mol. wt.	Molecular refractions Gladstone–Dale Calcd.	Found		Lorenz–Lorentz Calcd.	Found	
$HC(OCH_3)_3$	106.078	41.49	41.56	41.56	25.60	25.34	25.35
$HC(OC_2H_5)_3$	148.125	64.44	65.21	65.21	39.45	39.64	39.61
$HC(OCH(CH_3)_2)_3$	190.172	87.39	88.24	88.01	53.31	53.47	53.37
$HC(OCH_2CH_2CH_3)_3$	190.172	87.39	87.95	87.74	53.31	53.19	53.10
$HC(OCH_2CH(CH_3)_2)_3$	232.218	110.34	111.64	111.36	67.16	67.33	67.29
$HC(O(CH_2)_3CH_3)_3$	232.218	110.34	111.66	111.20	67.16	67.32	67.08
$HC(OC_5H_{11}$-*i*$)_3$	274.265	133.29	134.62	134.82	81.02	81.09	81.19

TABLE III

ANALYSES OF TRI-ALKYL ORTHOFORMATES

Tri-alkyl	Formula	Subs., g.	H_2O, g.	CO_2, g.	H, % Calcd.	Found	C, % Calcd.	Found
Methyl	$C_4H_{10}O_3$	0.1489	0.1286	0.2474	9.50	9.66	45.24	45.30
Ethyl	$C_7H_{16}O_3$	.1185	.1179	.2446	10.89	11.13	56.71	56.28
i-Propyl	$C_{10}H_{22}O_3$	.1481	.1525	.3411	11.66	11.52	63.10	62.81
n-Propyl	$C_{10}H_{22}O_3$	.0825	.0888	.1909	11.66	12.04	63.10	62.95
i-Butyl	$C_{13}H_{28}O_3$	.1498	.1658	.3668	12.15	12.38	67.17	66.77
n-Butyl	$C_{13}H_{28}O_3$	.1877	.1986	.4604	12.15	11.84	67.17	66.91
i-Amyl	$C_{16}H_{34}O_3$	.1033	.1189	.2636	12.49	12.88	69.98	69.61

sodium chloride was filtered off. The clear filtrate was fractionated at atmospheric pressure. The lower fractions consisted of unreacted chloroform and alcohol and could be used over again. The higher constant boiling fraction was collected and redistilled three times. The product was considered to be pure; yield, 30%. The simple physical constants were then determined.

Tri-alkyl orthoformates are colorless liquids with a faint characteristic odor, insoluble in water but soluble in all organic solvents. They could be distilled at atmospheric pressure without any decomposition.

Summary

1. Seven simple tri-alkyl orthoformates have been synthesized from chloroform and sodium alkoxides. Among these, the *i*-propyl and *n*-butyl ortho-esters are new compounds. The rest have been mentioned in the literature, but their simple physical constants are for the first time accurately determined.

PEIPING-WEST, CHINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

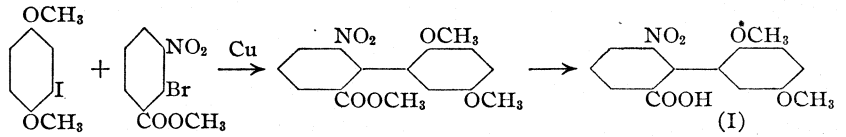
STEREOCHEMISTRY OF DIPHENYL. XXIII.[1] OPTICALLY ACTIVE 2,5-DIMETHOXY-2′-NITRO-6′-CARBOXYDIPHENYL AND THE MUTAROTATION OF ITS SALTS

BY H. C. YUAN[2] AND ROGER ADAMS

RECEIVED MARCH 17, 1932 PUBLISHED JULY 6, 1932

On the assumption that the size of the 2,2′,6,6′ groups is the primary factor in preventing free rotation of the aryl groups in substituted diphenyls, the relative rates of racemization of various derivatives should lead to conclusions concerning the relative size of groups. Since the tetra-substituted derivatives, except in very few instances, present molecules which cannot be racemized at all or only with great difficulty, the 2,2′,6-trisubstituted diphenyls offer the most promising field for this study.

In the present investigation a compound was selected containing one group, the methoxyl, which from previously published and unpublished results, was known to be small. The specific compound prepared was 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl (I).



(I)

[1] The last five papers in this series are as follows: (a) Hill and Adams, THIS JOURNAL, **53**, 3453 (1931); (b) Bock and Adams, *ibid.*, **53**, 3519 (1931); (c) Woodruff and Adams, *ibid.*, **54**, 1977 (1932); (d) Roll and Adams, *ibid.*, **54**, 2494 (1932); (e) White and Adams, *ibid.*, **54**, 2104 (1932).

[2] This communication is an abstract of a portion of a thesis submitted by H. C. Yuan in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

This acid was converted into a brucine salt in alcohol solution and the solid salt obtained by evaporation. It was then dissolved in hot water and in the course of a few days three-fourths of the total weight of the salt in solution was deposited in the form of a light yellow homogeneous crystalline compound. Upon evaporation of the filtrate, only the same salt could be obtained. It was thus obvious that, if a racemic acid were in hand at the beginning, the second salt during the period of crystallization or of the concentration of the liquors, was gradually converted to the less soluble form which, in turn, precipitated.

The brucine salt thus obtained showed a very interesting phenomenon. When dissolved in an organic solvent such as chloroform, a specific rotation was at first obtained, $[\alpha]_D^{25}$ $-167°$, which, over a period of time, changed gradually to a final value, $[\alpha]_D^{25}$ $+3.2°$, and then remained constant. This obviously presents a new example of mutarotation.[3] The resulting product was presumably an equal mixture of the salts from the *l*-brucine *d*-acid and the *l*-brucine *l*-acid, since the solid salt obtained from such a solution by precipitation with petroleum ether gave an inactive acid on decomposition with cold hydrochloric acid. If the original acid in chloroform or alcohol was mixed with a molecular quantity of brucine in the same solvent and made up to a known volume, rotations identical with the mutarotation values of the solid brucine salt in chloroform or alcohol were obtained. It was noticeable, however, that the final constant rotation did not appear at once but only after some minutes, especially in the case of dry chloroform.

The solid brucine salt was decomposed by ice-cold hydrochloric acid and the active acid thus obtained proved to be the *l*-modification. It racemized with unusual ease. At room temperature the time necessary to reach zero rotation was between sixty and seventy minutes, though at 0° the racemization was much slower. The half-life period was 10.8 min. at 28° and 274 min. at 0°. The *l*-modification showed the same melting point as the racemic acid, due, in all probability, to its conversion to the racemic acid before melting.

The sodium salts of all the previously studied optically active 2,2′,6,6′-substituted diphenyls, of which two of the groups were carboxyls, racemized in aqueous solution more readily than the free acid racemized in organic solvents. This was assumed to be due to ionization and the smaller size of the COO^- group, though the electrical characteristics of the ion might well be a factor in such experiments. Curiously enough, the sodium salt of 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl in water racemized less readily

[3] Meisenheimer, who found a somewhat similar phenomenon in 8,8′-dicarboxydinaphthyl, its monoethyl ester and 8-carboxydinaphthyl, prefers to speak of it as racemization. Meisenheimer and Beitswenger, *Ber.*, **65**, 32 (1932). See also Kuhn and Albrecht, *Ann.*, **455**, 272 (1927); **458**, 221 (1927); Kuhn, *Ber.*, **65**, 49 (1932); also Read and McMath, *J. Chem. Soc.*, 1572 (1925).

than the free acid in organic solvents. The sodium salt in absolute alcohol, however, racemized more readily than the free acid in the same solvent.

The cinchonine salt of 2,5 - dimethoxy - 2′ - nitro - 6′ - carboxydiphenyl showed similar characteristics to the brucine salt. It mutarotated from $[\alpha]_D^{23}$ −135° to $[\alpha]_D^{23}$ +57°. On the other hand, the strychnine salt showed no change of rotation in solution. This may have been due to a similar solubility of the two diastereoisomeric strychnine salts.

The rates of mutarotation of the salts, racemization of the acids, the half-life periods and the extrapolated maximum rotations are shown in the figures and table.

TABLE I

ROTATIONS OF BRUCINE *l*-SALT, CINCHONINE *l*-SALT AND *l*-2,5-DIMETHOXY-2′-NITRO-6′-CARBOXYDIPHENYL

$[\alpha]_D$: $l = 2$

Substance, g.	Solvent	Vol., cc.	Temp., °C.	Max. $[\alpha]_D$ by extrap.	Initial Time, min.	Initial $[\alpha]_D$	Final Time, min.	Final $[\alpha]_D$	Average K	Half-life period in min.	Average deviation of K
Brucine salt											
0.0467	Chloroform	10	25	−195°	4	−167°	98	+ 3.2°	0.018	16.8	±0.001
.0597	Abs. alc.	10	25	−165°	4	−119°	70	+ 3.7°	.028	10.8	± .002
.0361	Pyridine	10	25	−166°	4	−124°	60	−69°	.032	9.4	± .002
Cinchonine salt											
0.0480	Chloroform	10	23	−155°	4	−135°	120	+57°	.012	25.0	± .001
l-Acid											
0.1747	Abs. alc.	15	28	− 88°	4	− 74°	70	0.0	.028	10.8	± .002
.0315	Acetone	10	26	−124°	2	−112°	93	.0	.022	13.7	± .002
.0328	Acetic acid	10	26	− 88°	2	− 75°	50	.0	.035	8.6	± .002
.0340	Abs. alc.[a]	10	0	−136°	5	−135°	40 Hrs.	.0	.0011	274.0	.....
.0395	0.1 *N* NaOH Solution	10	26	−208°	3.5	−190°	160	.0	.011	27.4	± .001
.0291	Dil. NaOEt[b]	10	27	−289°	2	−195°	20	.0	.082	3.7	± .005

[a] In this experiment $l = 1$. [b] A solution of 0.5 g. of metallic sodium in 500 cc. of absolute alcohol was used for this purpose.

From the rotation values at different time intervals, the constant K of the rate of mutarotation can be calculated by the formula

$$K = \frac{1}{t} \log \frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$$

where α_t is time in minutes, α_0 the initial rotation, α_f the final rotation, α_t rotation at time t. The half-life period is calculated from the equation $T = (1/K) \log 2$.

If the assigned values of the relative size of the groups on the basis of x-ray data are approximately correct, the compound described in this investigation should be more stable than actually found.[4] Neither the 2′-carboxyl nor the 6′-nitro group should collide with the 2-hydrogen atom, but the interference on the other side of the molecule would be (assuming the value of the methoxyl the same as the hydroxyl), NO_2, 1.92 Å. + OCH_3, 1.54 Å. = 3.46 Å. −2.90 Å. = 0.56 Å.; COOH, 1.56 Å. + OCH_3,

[4] Stanley and Adams, THIS JOURNAL, **52**, 1200 (1930).

1.54 Å. = 3.10 Å. −2.90 Å. = 0.20 Å. Under these conditions the compound should be more stable to racemization if proper conclusions can be drawn from the data on compounds previously studied. It follows, therefore, that the methoxyl has a smaller value than originally assigned to it. A proposed value is 1.45 Å., which would lead to a slight interference between the methoxyl and carboxyl, the latter being the smaller of the nitro and carboxyl groups: COOH, 1.56 Å. + 1.45 Å. = 3.01 Å. −2.90 Å. = 0.11 Å. This value is slightly larger than that for the fluorine atom which has been directly determined by x-rays and therefore represents probably a fairly correct value.

The 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl was prepared by condensation with copper of 1-nitro-2-bromo-3-carbomethoxybenzene and 2-iodo-1,4-dimethoxybenzene followed by saponification of the product.

The combination of nitro, carboxyl and hydrogen with another grouping in the 2,2′,6,6′-positions is an ideal one for further study since the relative racemization rates can be studied in a reasonably quantitative way. A series of compounds containing the nitro, carboxyl, hydrogen and the halogens, F, Cl and Br and other groups are being prepared and the results will soon be ready for publication. From these compounds conclusions concerning the relative size of the F, Cl, Br, OCH_3, CH_3, carboxyl and nitro groups will be possible. The combination of nitro, carboxyl, methoxyl and hydrogen also offers the possibility of determining whether the presence of substituting groups in other positions in the molecule will affect the rate of racemization of molecules in which the 2,2′,6,6′ groups remain the same.

Experimental

2,5-Dimethoxy-2′-nitro-6′-carboxydiphenyl.—In a 200-cc., three-necked flask fitted with a mechanical stirrer and an air condenser were placed 40 g. of 1-iodo-2,5-dimethoxybenzene[5] and 15 g. of 1-nitro-2-bromo-3-carbomethoxybenzene. Then the flask was gradually heated in a metal bath to 260°, at which temperature the decomposition of the iodo compound to give off iodine vapor was noticed. In small portions, 30 g. of copper bronze was now introduced. Each addition of copper resulted in a rise of temperature sufficient to cause the temporary boiling of the reaction mixture. The addition of all of the copper required about fifty minutes, and during this period the bath temperature was maintained at 260–270°. After all of the copper was added, the bath temperature was raised to 300° to reflux the reaction mixture for twenty minutes. The flask was removed from the bath and cooled. The products were then extracted with 200 cc. of ether. From the ether, by evaporation, a dark oily residue resulted which was transferred to a 500-cc. flask and refluxed with 200 cc. of 5% aqueous sodium hydroxide for four hours. The unsaponifiable oil was separated from the water solution and the water layer was shaken with two 50-cc. portions of ether to remove some tarry substance which was present. The solution was then acidified with dilute hydrochloric acid. An oily substance separated out immediately and solidified upon standing or cooling. It was a mixture of dinitrodiphenic acid and 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl and weighed 16 g. The crude product was then dissolved in 60 cc. of warm

[5] Kauffmann and Fritz, *Ber.*, **41**, 4413 (1908).

glacial acetic acid and treated with some norite. Upon standing for several hours, 1.5 g. of white crystalline substance was obtained which proved to be 2,2′-dinitro-6,6′-diphenic acid. The mother liquor was diluted with an equal amount of water and decanted from the tarry substance which separated. Another 60 cc. of water was added and the solution was heated to bring all the precipitate to solution. Light yellow long crystals were obtained after standing at room temperature overnight. About half a gram of the same product could be obtained from the tar by extraction with 250 cc. of boiling water. They were combined and recrystallized twice from 20% alcohol. The yield was 5 g.

The 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl forms lemon-yellow leaflets. It melts at 141–142°. It is very soluble in the common organic solvents except carbon tetrachloride, petroleum ether and slightly soluble in chloroform and hot water.

Anal. Calcd. for $C_{15}H_{13}NO_6$: Neut. equiv., 303.1; N, 4.62. Found: Neut. equiv., 305.8; N (Micro Dumas), 4.80.

Alkaloid Salts of 2,5-Dimethoxy-2′-nitro-6′-carboxydiphenyl. (Brucine Salt.)—A solution of 0.933 g. of 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl in 10 cc. of alcohol was treated with a solution of 1.292 g. of brucine in 20 cc. of alcohol. No salt was obtained upon cooling, or upon dilution with water or with ethyl acetate. It was then evaporated to dryness and a granular residue was left. The residue was dissolved in 240 cc. of boiling water. Upon standing at room temperature overnight, 1.4 g. of the brucine salt was obtained as slightly yellow short needles. By concentrating the mother liquor to 100 cc., 0.3 g. more of salt was obtained. A third portion of 0.4 g. was obtained by evaporating the mother liquor to dryness at room temperature. Different portions of the salts were identical. Each fraction had the same melting point, 158–160°, the same maximum specific rotation, the same mutarotation. It had one mole of water of crystallization.

Anal. Calcd. for $C_{38}H_{39}N_3O_{10}\cdot H_2O$: H_2O, 2.52; N (anhydrous salt), 6.03. Found: H_2O, 2.26; N, 6.16.

Mutarotation Experiments.[6] **(See Fig. 1 and Table I.)**—Racemic acid was dissolved in chloroform and neutralized with a molecular equivalent of brucine in chloroform. A similar experiment was performed in alcohol. In both instances the constant rotation was, within experimental error, the same as the mutarotation value of the isolated salt dissolved in the same solvent. In these experiments the final reading was not reached immediately.[7] This may have been due to the slowness in salt formation in the organic solvent. It was not due to the fact that the mixture at the equilibrium point consisted of unequal quantities of *l-l* and *l-d* salts because the salt at this point was precipitated completely by addition of petroleum ether and, upon decomposition in the manner found suitable for obtaining active acid from the *l-l* salt, gave only inactive acid.

0.1673 g. of the racemic acid and 0.2130 g. of anhydrous brucine made up to 50 cc. with chloroform gave an initial rotation (four minutes after preparation) α_D −0.13; $l = 2$, $[\alpha]_D^{25}$ −8.6°. After eighty minutes $[\alpha]_D$ + 0.05°; $[\alpha]_D^{25}$ +3.3°. A second experiment required even a longer time for equilibrium to be reached.

0.9330 g. of the racemic acid and 1.2920 g. of anhydrous brucine made up to 45 cc. with absolute alcohol gave an initial rotation (fourteen minutes after preparation) α_D +2.6°, $[\alpha]_D^{26}$ 2.6°, but it required another hour before α_D +0.30; $[\alpha]_D^{26}$ +3.0°.

[6] The numerous intermediate α_D readings are not recorded but the values found are shown in the curves in the charts.

[7] Mills and Elliot, *J. Chem. Soc.*, 1291 (1928), observed the same phenomenon in N-benzenesulfonyl-8-nitro-1-naphthylglycine.

The brucine salt could be dehydrated in the usual way and gave a rotation comparable to that of the hydrated form.

0.0951 g. of salt heated at 100° for five hours made up to 15 cc. with chloroform at 25° (two minutes after preparation) gave α_D −2.05°; l = 2, $[\alpha]_D^{25}$ −162°. By extrapolation this corresponds to $[\alpha]_D^{25}$ −195° for hydrated salt, which is within experimental error of the found value.

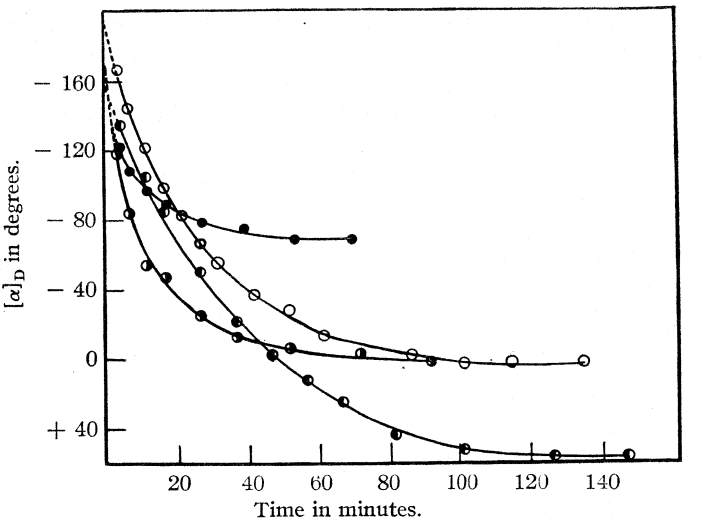


Fig. 1.—Mutarotation curves of brucine and cinchonine salts of 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl in various solvents. The dotted lines indicate values by extrapolation: ○, brucine salt in chloroform at 25°; ◑, brucine salt in ethanol at 25°; ●, brucine salt in pyridine at 25°; ◐, cinchonine salt in chloroform at 23°.

Attempts were made to isolate the other *l*-brucine *d*-acid salt by extracting the filtrate from the *l*-brucine *l*-acid salt which had crystallized out of aqueous solution. The ice-cold filtrate was extracted with ice-cold chloroform and the chloroform solution run immediately into a large volume of petroleum ether. All the brucine salt precipitated but gave a rotation corresponding to the equilibrium rotation value $[\alpha]_D^{25}$ +3.0° in spite of the fact that the whole operation of extraction and precipitation took less than five minutes.

Cinchonine Salt.—A solution of 0.6035 g. of 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl in 10 cc. of methanol was treated with 0.5864 g. of cinchonine in 30 cc. of boiling methanol. After standing at room temperature overnight, 0.42 g. of the cinchonine salt crystallized out as light yellow small needles. From the mother liquor after two days in the ice box, a second portion of the salt separated which weighed 0.35 g. The filtrate from this material upon evaporation gave a further quantity of salt. The different portions of the salt had the same melting point, 198–204° and mutarotated at the same rate.

Anal. Calcd. for $C_{34}H_{35}N_3O_7$: N, 7.03. Found: N (micro Dumas), 7.21.

Strychnine Salt.—A solution of 0.4819 g. of 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl in 8 cc. of absolute alcohol was mixed with 0.5314 g. of strychnine in 45 cc. of

boiling alcohol. No crystals were obtained after long standing. The solution was evaporated to dryness and the granular residue was dissolved in 85 cc. of boiling water. Upon standing at room temperature for several hours, 0.38 g. of the strychnine salt crystallized out as compact plates. Two more portions were obtained by further concentration of the solution. They had the same melting point, 220–223° with decomposition, and the same specific rotation. Unlike the other salts, it showed no mutarotation.

A solution of 0.0715 g. made up to 10 cc. with chloroform at 23° gave a rotation α_D −0.33°; l = 2, $[\alpha]_D^{23}$ −23.1.

Anal. Calcd. for $C_{38}H_{35}N_3O_8$: N, 6.59. Found: N (micro Dumas), 6.75.

The acid obtained from the strychnine salt by the procedure described under the brucine salt was inactive.

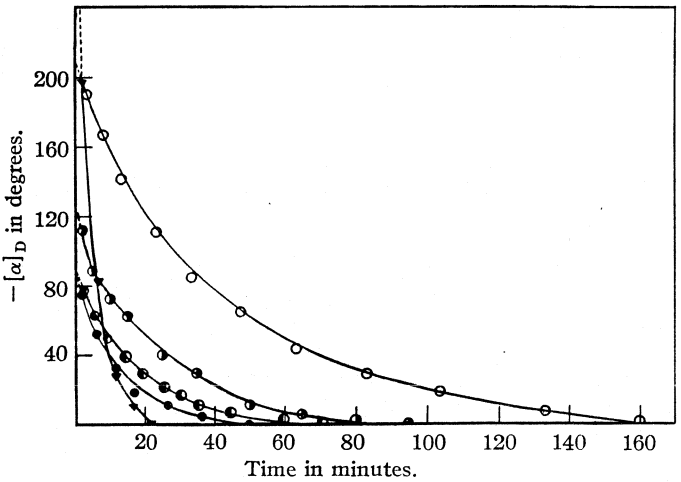


Fig. 2.—Racemization curves of *l*-2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl and its sodium salt. The dotted lines indicate values by extrapolation: ◐, *l*-acid in ethanol at 28°; ◑, *l*-acid in acetone at 26°; ●, *l*-acid in acetic acid at 26°; ○, sodium salt in water at 26°; ▼, sodium salt in ethanol at 26°.

l-2,5-Dimethoxy-2′-nitro-6′-carboxydiphenyl.—A suspension of 1 g. of the brucine salt in ice-cold 100 cc. 6 *N* hydrochloric acid surrounded with ice–salt mixture was stirred vigorously for a half hour. Then it was left in the ice box overnight. The next morning, finely divided 2,5-dimethoxy-2′-nitro-6′-carboxydiphenyl, which is darker yellow than the salt, had settled to the bottom. The acid was then filtered by suction and washed thoroughly with ice-cold water until the filtrate showed negative tests for both brucine and chloride. The dried acid weighed 0.41 g. It melted at 141–142°.

Racemization Experiments.[6]—See Fig. 2 and Table I.

Summary

1. 2,5-Dimethoxy-2′-nitro-6′-carboxydiphenyl was prepared by condensation of 1-iodo-2,5-dimethoxybenzene and 1-nitro-2-bromo-3-carbomethoxybenzene with copper, and saponification of the product.

2. The acid readily forms brucine and cinchonine salts. Only one salt

with each alkaloid could be isolated. Each of the salts mutarotated to equilibrium values which were equal mixtures of the two diastereoisomeric salts. Strychnine gave a salt which showed no mutarotation and yielded no active acid.

3. By careful decomposition with hydrochloric acid, the *l*-acid was isolated. It racemized rapidly in organic solvents. The sodium salt racemized much more rapidly in absolute alcohol than in water.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

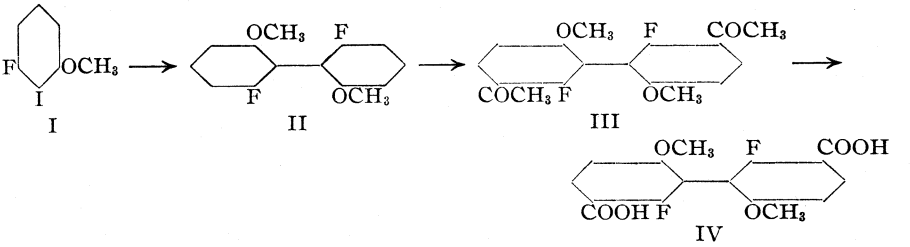
STEREOCHEMISTRY OF DIPHENYL. XXIV.[1] PREPARATION AND PROPERTIES OF 2,2′-DIFLUORO-3,3′-DICARBOXY-6,6′-DIMETHOXYDIPHENYL

BY B. C. BECKER[2] AND ROGER ADAMS

RECEIVED MARCH 17, 1932 PUBLISHED JULY 6, 1932

The small size of the fluorine atom and, as shown in the previous paper, the similarly small size of the methoxyl group,[1e] made particularly interesting a study of the properties of properly substituted 2,2′,6,6′-tetrafluoro-, 2,2′,6,6′-tetramethoxy- and 2,6-difluoro-2,6′-dimethoxydiphenyls. On the assumption that the methoxyl is about the same size as the fluorine and calculating the interference possibilities as previously described,[3] none of these three compounds should be capable of resolution.

A representative of the last type has been prepared and is described in this communication. The compound is 2,2′-difluoro-3,3′-dicarboxy-6,6′-dimethoxydiphenyl (IV).



It was prepared (1) by the condensation with copper of 1-fluoro-2-iodo-3-methoxybenzene to 2,2′-difluoro-6,6′-dimethoxydiphenyl (II), (2) by in-

[1] The last five papers in this series are as follows: (a) Hill and Adams, THIS JOURNAL, **53**, 3453 (1931); (b) Woodruff and Adams, *ibid.*, **54**, 1977 (1932); (c) White and Adams, *ibid.*, **54**, 2104 (1932); (d) Roll and Adams, *ibid.*, **45**, 2494 (1932); (e) Yuan and Adams, *ibid.*, **54**, 2966 (1932).

[2] This communication is a portion of a thesis submitted by B. C. Becker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Stanley and Adams, THIS JOURNAL, **52**, 1200 (1930).

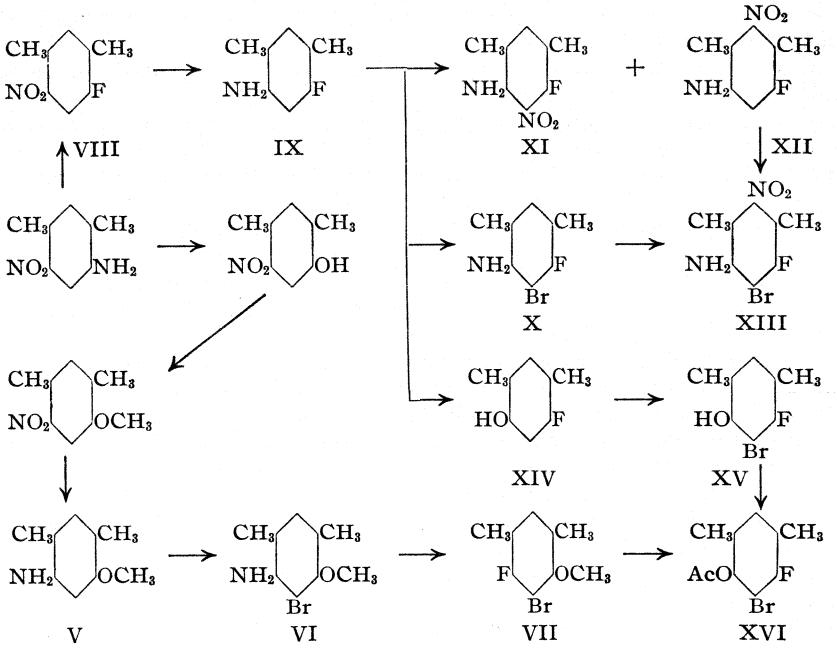
troduction of two aceto groups by means of aluminum chloride and acetyl chloride to 2,2′-difluoro-3,3′-diaceto-6,6′-dimethoxydiphenyl (III), (3) by oxidation of the diaceto derivative by means of sodium hypochlorite to 2,2′-difluoro-3,3′-dicarboxy-6,6′-dimethoxydiphenyl (IV). The various alkaloid salts—brucine, strychnine, morphine, cinchonine and quinine—were all prepared. In no instance was more than a single salt obtained and none of these showed mutarotation even at low temperatures or gave an active acid on decomposition. It appears then that this is truly a representative of a 2,2′,6,6′-tetrasubstituted diphenyl in which the ortho substituents do not interfere sufficiently to allow resolution.

Before the above compound was prepared, a number of proper intermediate compounds were synthesized, but all attempts to convert them to the corresponding diphenyls were unsuccessful. These will be described briefly. It was found impossible to obtain 1-fluoro-2-nitro-3-methoxybenzene from 1-fluoro-3-methoxybenzene by nitrating according to the procedure found successful for nitrating 1-fluoro-3-hydroxybenzene.

1-Fluoro-2,4-dimethyl-5-methoxy-6-bromobenzene (VII) was prepared by bromination of 1-amino-2,4-dimethyl-5-methoxybenzene (V) and replacement of the amino group in the 1-amino-2,4-dimethyl-5-methoxy-6-bromobenzene (VI) by fluorine. From the product (VII) attempts to fill the last position in the ring with a nitro or aceto group, to form the Grignard reagent, or to carry out an Ullmann reaction were all unsuccessful.

1-Fluoro-2,4-dimethyl-5-nitrobenzene (VIII) was prepared from the corresponding amino compound by introduction of a fluorine in place of the amino group. It was converted by reduction to 1-fluoro-2,4-dimethyl-5-aminobenzene (IX), which was brominated to 1-fluoro-2,4-dimethyl -5 - amino - 6 - bromobenzene (X). 1 - Fluoro - 2,4 - dimethyl - 5 - aminobenzene (IX) was nitrated in sulfuric acid to a mixture of the 1-fluoro - 2,4 - dimethyl - 5 - amino - 6 - nitrobenzene (XI) and 1 - fluoro - 2,4 - dimethyl - 5 - amino - 3 - nitrobenzene (XII). The 1 - fluoro - 2,4 - dimethyl-5-amino-3-nitrobenzene (XII) was then brominated to 1-fluoro-2,4-dimethyl-3-nitro-5-amino-6-bromobenzene (XIII), identical with the product obtained by nitration of 1-fluoro-2,4-dimethyl-5-amino-6-bromobenzene (X). Attempts to replace the amino group in 1-fluoro-2,4-dimethyl-3-nitro-5-amino-6-bromobenzene (XIII) by hydroxyl or methoxyl were unsuccessful, though no difficulty was encountered in replacing the amino group by chlorine.

1-Fluoro-2,4-dimethyl-5-aminobenzene (IX) was diazotized and converted to 1-fluoro-2,4-dimethyl-5-hydroxybenzene (XIV) which was brominated to 1-fluoro-2,4-dimethyl-5-hydroxy-6-bromobenzene (XV). This product gave an acetyl derivative (XVI), identical with that obtained by demethylating and acetylating 1-fluoro-2,4-dimethyl-5-methoxy-6-bromobenzene (VII).



Experimental[4]

1-Fluoro-2-iodo-3-methoxybenzene.[5]—This product has been described by Hodgson and Nixon. In this investigation it was prepared by the same series of reactions, 3-nitroaniline ⟶ 1-fluoro-3-nitrobenzene ⟶ 1-fluoro-3-aminobenzene ⟶ 1-fluoro-3-hydroxybenzene ⟶ 1-fluoro-2-nitro-3-hydroxybenzene ⟶ 1-fluoro-2-nitro-3-methoxybenzene ⟶ 1-fluoro-2-amino-3-methoxybenzene ⟶ 1-fluoro-2-iodo-3-methoxybenzene. Since the previous authors give no details, a comment or two on each step may be serviceable to others.

3-Nitroaniline was converted into the corresponding diazonium fluoborate in the usual way. The yield was 79%. The product, light brown crystals in crude form, could be purified by dissolving in methyl alcohol and precipitating with ethyl ether. White crystals were formed which decomposed at 170–175° after darkening at 145°.

The fluoborate was decomposed as slowly as possible by careful heating *in vacuo*, then by heating thoroughly to drive over all the product. After alkali washing and steam distillation, a 50% yield of 1-fluoro-3-nitrobenzene of b. p. 197–202° at 750 mm. was obtained.

1-Fluoro-3-nitrobenzene was reduced in the usual way with iron powder and water in the presence of a little hydrochloric acid. The mixture after neutralization was steam-distilled; yield, 85%, b. p. 185° at 755 mm.

1-Fluoro-3-aminobenzene was converted to the corresponding phenol by following

[4] The melting points reported in this investigation are uncorrected.

[5] Hodgson and Nixon, *J. Chem. Soc.*, 880 (1928); *ibid.*, 981 (1931); Swarts, *Bull. acad. roy. Belg.*, 241 (1913); Schiemann and Pillarsky, *Ber.*, **62**, 3035 (1929). The literature constants are as follows: 1-fluoro-3-nitrobenzene, b. p. 200° at 756 mm., m. p. 3.6°; 1-fluoro-3-aminobenzene, b. p. 186° at 753 mm.; 1-fluoro-3-hydroxybenzene, b. p. 177.8° at 760 mm., m. p. 13.7°; 1-fluoro-2-iodo-3-methoxybenzene, b. p. 240° at 756 mm.

the directions of Hodgson and Nixon used for 3-chloro-1-hydroxybenzene;[6] yield, 76%, b. p. 174° at 753 mm.

1-Fluoro-2-nitro-3-hydroxybenzene was obtained in 50% yield; orange yellow needles, m. p. 39°.

1-Fluoro-2-nitro-3-methoxybenzene was prepared by methylating in dry xylene solution with anhydrous potassium carbonate and dimethyl sulfate. Addition of water and then distillation of most of the xylene gave a product, readily purified from methyl alcohol and then petroleum ether; yield, 80% of white crystals, m. p. 43°.

1-Fluoro-2-amino-3-methoxybenzene was prepared by reduction of a methyl alcoholic solution of the nitro compound with concentrated hydrochloric acid and stannous chloride. It was then made alkaline, steam distilled and extracted with ether. The hydrochloride was precipitated with hydrogen chloride after drying the ether solution; yield of amine hydrochloride 81%.

1-Fluoro-2-iodo-3-methoxybenzene was made from the amine hydrochloride by diazotizing and treating with potassium iodide. The product was extracted with ether and washed with sodium bisulfite; yield, 65%, b. p. 115–125° at 3–6 mm.

2,2′-Difluoro-6,6′-dimethoxydiphenyl.—A mixture of 25 g. (0.1 mole) of 1-fluoro-2-iodo-3-methoxybenzene and 25 g. of copper bronze was placed in a small Pyrex flask fitted with a short air condenser and heated in a metal bath at 180–200° for one hour or until the odor of the iodo compound was no longer detectable. The coupling took place much more rapidly at 210–220° but the yield was slightly less. After the flask had cooled sufficiently, the contents were extracted with 40-cc. portions of hot ethyl alcohol. The alcohol was filtered and allowed to cool. Yellow-white crystals of difluorodimethoxydiphenyl were deposited. Evaporation of the mother liquor gave additional crystals which were more yellow. The total yield of crude product was 10 g. (80%). After recrystallization from petroleum ether and again from ethyl alcohol, there remained 8 g. (65%). By several more recrystallizations from ethyl alcohol, pure white 2,2′-difluoro-6,6′-dimethoxydiphenyl was obtained. It melted at 135–136°.

Anal. (Micro). Calcd. for $C_{14}H_{12}F_2O_2$: C, 67.2; H, 4.84. Found: C, 67.23; H, 4.85.

2,2′-Difluoro-3,3′-diaceto-6,6′-dimethoxydiphenyl.—In a three-necked flask fitted with a mercury-sealed stirrer, a lead to a water trap, and a stopper, 5 g. (0.02 mole) of difluorodimethoxydiphenyl was dissolved in a mixture of 75 cc. of dry carbon disulfide and 25 cc. of acetyl chloride. The solution was cooled in a salt-ice mixture and three 5-g. portions of powdered anhydrous aluminum chloride were introduced at ten-minute intervals. The stirring was continued after the ice-bath had been removed until the contents of the flask had reached room temperature. The carbon disulfide top layer was then decanted from the viscous lower layer which was washed with a fresh portion of carbon disulfide. The lower layer containing the aluminum chloride was slowly poured onto 250 g. of cracked ice. The diacetodifluorodimethyldiphenyl readily formed a solid mass suspended in the water solution of the aluminum chloride. The solid was filtered and washed repeatedly with water to remove all of the inorganic salts. The yield of the crude material was quantitative (6.7 g.) but was reduced to 90% after recrystallization from methyl alcohol. The diacetodiphenyl formed white crystals melting at 138–139.5°.

Anal. Calcd. for $C_{18}H_{16}F_2O_4$: C, 64.65; H, 4.83. Found: C, 64.92; H, 4.78.

2,2′-Difluoro-3,3′-dicarboxy-6,6′-dimethoxydiphenyl.—The difluorodimethoxydiphenyl was oxidized to the difluorodicarboxydimethoxydiphenyl by means of sodium hypochlorite, according to the general procedure of VanArendonk and Cupery.[7]

[6] Hodgson, English Patent, 200,714 (1923).

[7] VanArendonk and Cupery, THIS JOURNAL, **53**, 3184 (1931).

A solution of 6.7 g. (0.02 mole) of difluorodiacetodimethoxydiphenyl in 250 cc. of methyl alcohol was made alkaline with 20 cc. of 20% sodium hydroxide. This solution was kept cold while alkaline sodium hypochlorite was added slowly. (The sodium hypochlorite was prepared from two 100-cc. portions of 20% sodium hydroxide by passing in chlorine gas in the cold until the reaction to litmus was neutral. A liberal excess (20–30 cc.) of sodium hydroxide was then added to make the solution markedly basic.) Keeping the solutions alkaline and cold (under 30°) was important in preventing ring chlorination. As the sodium hypochlorite solution was added, a cloudiness was produced which disappeared as the diphenic acid was formed from the ω-chlorinated aceto derivative. Before acidifying, the excess hypochlorite was destroyed by bubbling in sulfur dioxide or by adding sodium bisulfite until the solution no longer reacted to starch–iodide paper when acidified. Upon acidification the acid was precipitated as a solid, which was filtered off. Additional acid was obtained from the filtrate by making it alkaline, evaporating the methyl alcohol, and reacidifying. The yield was 5.7 g. (84%). The crude acid was purified by dissolving in sodium hydroxide solution, boiling with norite, and reprecipitating. It could also be crystallized from methyl alcohol; m. p 285–289° with decomposition. For analysis the acid was dried at 110° for twelve hours.

Anal. Calcd. for $C_{16}H_{12}F_2O_6$: neut. equiv., 169; C, 56.8; H, 3.58. Found: neut. equiv., 173.5; C, 56.9; H, 3.71.

Alkaloid Salts of 2,2′-Difluoro-6,6′-dimethoxy-3,3′-dicarboxydiphenyl

Brucine Salt.—When 0.58 g. of anhydrous brucine dissolved in 30 cc. of ethyl alcohol was added to 0.50 g. of the diphenic acid in 80 cc. of ethyl alcohol, a white amorphous precipitate was formed. This weighed 0.86 g. or 80% of the calculated total weight of salt formed. There was no loss of weight on heating to 110° *in vacuo*, hence no solvation.

Rotation. 0.0205 g. made up to 5.4 cc. with pyridine gave α_D −0.26°; $l = 1$; $[\alpha]^{25}_D$ −68.5°.

The monobrucine salt was also prepared in ethyl acetate in a similar manner. A distinctly crystalline product formed to the amount of 70% in the first fraction. The weight of the residual material brought the total to 82%. The crystalline fraction 0.0226 g. made up to 10 cc. with pyridine gave α_D 0.31°; $l = 2$; $[\alpha]^{25}_D$ −68.7°. The residual fraction gave $[\alpha]^{25}_D$ −61.4°. The first fraction was washed with warm dry ethyl acetate and dried.

Rotation. 0.0205 g. made up to 10 cc. with pyridine gave α_D −0.27°; $l = 2$; $[\alpha]^{25}_D$ −65.8°.

Anal. (Micro). Calcd. for $C_{39}H_{38}F_2N_2O_{10}$: N, 3.83. Found: N, 3.92.

Decomposition of the salt was carried out at 0–5°. A solution of 0.1 g. of the monobrucine salt in 30 cc. of chloroform was shaken with 100 cc. of ice water to which 2 cc. of concentrated hydrochloric acid had been added. The free diphenic acid was insoluble in both layers and was precipitated as fast as it was formed. After fifteen minutes of shaking the suspension was filtered and the free acid was dried over calcium chloride in a vacuum desiccator. The weight was 0.041 g. (calcd. 0.046). The acid was essentially pure, m. p. 280°, and was used without recrystallization. It gave no rotation in pyridine.

An attempt was made to determine if the newly formed salt showed any evidence of mutarotation. Into a 1-dm. rotation tube enclosed in case for cooling or heating, 0.0394 g. of anhydrous brucine dissolved in 7 cc. of pyridine was introduced. Rotation was taken at 25° and again at 0°, α_D −0.70° and −0.71°; $[\alpha]^{25}_D$ −124° and $[\alpha]^{0}_D$ −128°. Then, still at 0°, 0.0388 g. (0.005 g. excess) of the diphenic acid was introduced, mixed thoroughly, and a rotation was taken within a period of five minutes: α_D −0.535°;

$[\alpha]^0_D$ −51.2°. Rotation, three hours later: α_D −0.535°; $[\alpha]^0_D$ −51.2°. The tube and its contents were then permitted to warm to room temperature: α_D −0.663°; $[\alpha]^{25}_D$ −63.4°. (This checks the rotation of the crystalline monobrucine salt.) After twenty-four hours at room temperature the solution was again cooled to 0°. Rotation: α_D −0.540°; $[\alpha]^0_D$ −51.7°.

No success was encountered in attempting to prepare the dibrucine salt.

Morphine Salt.—The monobasic morphine salt was formed in dry ethyl acetate by the addition of 0.285 g. (0.001 mole) of morphine in 40 cc. of ethyl acetate to 0.338 g. of the diphenic acid in 80 cc. of ethyl acetate. The first fraction separated immediately and amounted to 0.25 g. or 40% of the total weight of salt; the second precipitate was obtained by partial evaporation and cooling, and weighed 0.128 g. (20%). The third fraction, formed on further evaporation, was 14%; and the residue recovered on evaporation to dryness was 10%. The specific rotations of these crude fractions, in 95% ethyl alcohol (l = 2) were, respectively, −63.5, −59.5, −64.3 and −26°. The low value for the residue was undoubtedly the result of impurities. The first two fractions (0.30 g.) were dissolved in absolute ethyl alcohol, filtered and cooled in carbon dioxide snow. A white precipitate was formed, weighing 0.17 g. and having a coarsely granular appearance under the microscope. A sample of this was dissolved in 95% ethyl alcohol at 0–10° and cooled immediately to 0°.

Rotation. 0.0243 g. made up to 10 cc. with ethyl alcohol at 0° gave α_D −0.20°; l = 1; $[\alpha]^0_D$ −82.3°.

The solution in the rotation tube was allowed to come to room temperature 25°: α_D −0.145°; $[\alpha]^{25}_D$ −59.7°. (This checked the rotation of crude fractions.) The solution was further allowed to stand at 25–30° for twenty hours and then cooled again to 0°: α_D −0.19°; $[\alpha]^0_D$ −78.2°. Analysis of the recrystallized material showed it to be the desired morphine salt.

Anal. (Micro). Calcd. for $C_{33}H_{31}F_2NO_9$: N, 2.25. Found: N, 2.4.

Quinine Salt.—A solution of 0.324 g. of quinine (0.001 mole) in 30 cc. of absolute ethanol was added to 0.338 g. of the diphenic acid dissolved in 30 cc. of absolute alcohol. Evaporation to half volume gave a yellow precipitate weighing 0.05 g. The second fraction, which was a very light yellow amorphous precipitate, weighed 0.26 g. The third or residual fraction was obtained by evaporation to dryness. It was quite yellow and weighed 0.217 g. The total recovered material amounted to 80% of the calculated value. These three fractions gave, respectively, the specific rotations in chloroform at 27°: −69.4, −83.4 and −75.4°. The intermediate fraction, 0.0736 g., made up to 10 cc. with chloroform gave α_D 1.23; l = 2; $[\alpha]^{27}_D$ −83.4°. This fraction was analyzed.

Anal. (Micro). Calcd. for $C_{38}H_{38}F_2N_2O_8$: N, 4.23. Found: N, 4.21..

Strychnine Salt.—A solution of 0.334 g. (0.001 mole) of strychnine in 50 cc. of absolute ethanol was added to 0.338 g. of the diphenic acid dissolved in absolute alcohol. The solution was filtered, evaporated to 40 cc., and cooled with carbon dioxide snow. A precipitate formed and was filtered off. However, on warming to room temperature this material melted and became viscous and sticky. On being placed in a desiccator, it finally hardened to a glassy solid which could be pulverized to a white amorphous powder; weight, 0.101 g.

Rotation. 0.0705 g. made up to 10 cc. with chloroform gave α_D −0.15°; l = 2; $[\alpha]^{25}_D$ −10.6°.

The second fraction of the strychnine salt was obtained by evaporating the ethyl alcohol to about 10 cc. and then adding 70 cc. of ethyl acetate. A white amorphous powder was precipitated. This was filtered off, washed with warm dry ethyl acetate and dried; weight, 0.422 g. (63%). On heating this salt shrank at 180–205° and foamed without darkening at 205–220°.

Rotation. 0.0627 g. made up to 10 cc. with chloroform gave α_D −0.15; $l = 2$; $[\alpha]_D^{25}$ −12°.

Analysis of the intermediate fraction showed it to be the desired salt. The residue soluble in ethyl acetate was negligible—the amount recovered being too small for a determination of the specific rotation.

Anal. (Micro). Calcd. for $C_{37}H_{34}F_2N_2O_8$: N, 4.16. Found: N, 4.25.

The intermediate fraction of strychnine salt, 0.2 g., was shaken with 50 cc. of 6 *N* hydrochloric acid at −15°. After two hours, the 6 *N* acid was replaced by a fresh 50-cc. portion—the free diphenic acid was filtered off, resuspended in cold hydrochloric acid, and placed in the refrigerator overnight. The free acid was then filtered off, washed free of hydrochloric acid, and dried at room temperature in a vacuum desiccator; weight, 0.093 g. (calcd. 0.101 g.); m. p. 275°. It showed no rotation.

Cinchonine Salt.—A solution of 0.294 g. (0.001 mole) of cinchonine in 30 cc. of absolute ethyl alcohol was added to 0.338 g. of the diphenic acid dissolved in 30 cc. of absolute alcohol. The solution was filtered, evaporated to 15 cc. and 50 cc. of ethyl acetate was added. A precipitate was formed, weighing 0.43 g.

Rotation. 0.0654 g. made up to 10 cc. with 95% ethyl alcohol gave α_D +1.08°; $l = 2$; $[\alpha]_D^{25}$ 82.7°.

The filtrate was evaporated to dryness to give a yellow amorphous material weighing 0.189 g.

Rotation. 0.0490 g. made up to 10 cc. with 95% ethyl alcohol gave α_D 0.75°; $l = 2$; $[\alpha]_D^{25}$ 76.5°.

Another run of 0.294 g. of cinchonine and 0.338 g. of acid in 60 cc. of absolute alcohol gave three fractions on the slow evaporation of the alcohol. Of these, the intermediate fraction, weighing 0.114 g. was white and amorphous.

Rotation. 0.0436 g. made up to 10 cc. with ethyl alcohol gave α_D 0.733°; $l = 2$; $[\alpha]_D^{25}$ 84.1°. Analysis of this fraction showed it to be the desired monocinchonine salt.

Anal. (Micro). Calcd. for $C_{35}H_{34}F_2N_2O_7$: N, 4.43. Found: N, 4.30.

1-Fluoro-3-methoxybenzene.—A solution of 123 g. (1 mole) of 1-amino-3-methoxybenzene in a mixture of 280 cc. of concentrated hydrochloric acid, and 500 g. of ice was diazotized at 0–5° by the addition of 69 g. of sodium nitrite in 160 cc. of water. The diazotized mixture was filtered if necessary and a minimum of 170 cc. of fluoboric acid solution was added. The precipitated diazonium fluoborate of 1-amino-3-methoxybenzene was filtered off and washed successively with 10–20 cc. of fluoboric acid solution, 70 cc. of ethyl alcohol, and 70 cc. of ethyl ether. The weight of dry diazonium salt was 170 g. (76%). This was quite unstable as compared with the corresponding 3-nitrodiazonium salt and unless it was kept very dry, it decomposed spontaneously over a period of twenty-four to forty-eight hours.

The diazonium salt was decomposed immediately without purification in a dry flask connected through a condenser and wash bottle to a water aspirator. Heat was applied to one part of the flask to start the decomposition; and the reaction was allowed to proceed spontaneously. Sometimes cooling was necessary if decomposition was too rapid. Finally, when the reaction subsided, the flask was heated strongly while the system was evacuated. The distillate and the water in the wash bottles were mixed, neutralized with sodium carbonate, filtered and extracted with ethyl ether. The 1-fluoro-3-methoxybenzene (b. p. 158° at 743 mm.) was a colorless mobile liquid of characteristic anisole-like odor. The yield was 53 g. (42%); d_{20}^{20} 1.107, n_D^{20} 1.4892.

Anal. (Micro). Calcd. for C_7H_7FO: C, 66.6; H, 5.60. Found: C, 66.77; H, 5.52.

1-Fluoro-2-nitro-3-methoxybenzene.—Attempts to prepare 1-fluoro-2-nitro-3-methoxybenzene by sulfonation and nitration of 1-fluoro-3-methoxybenzene as de-

scribed for the preparation of 1-fluoro-2-nitro-3-hydroxybenzene from 1-fluoro-2-nitro-3-hydroxybenzene were unsuccessful.

1-Amino-2,4-dimethyl-5-methoxy-6-bromobenzene Hydrobromide.—To a solution of 50 g. (0.33 mole) of 1-amino-2,4-dimethyl-5-methoxybenzene[8] in 250 cc. of glacial acetic acid, was added slowly 53 g. of bromine in 25 cc. of acetic acid. On cooling the mixture, fine white crystals of the brominated amine hydrobromide were precipitated. The precipitate was filtered and washed with 25–50 cc. of glacial acetic acid. The salt was dried at 110°. The yield depended upon the volume of acetic acid used; the pure product usually weighed about 78 g. (75%); m. p. 187° with decomposition. By evaporation of the acetic acid filtrate, the remaining impure material could be obtained. (Acetyl derivative of the free base, from dilute alcohol, m. p. 147–148°.) A small amount of the acetyl derivative was always formed when recrystallizing the amine hydrobromide from glacial acetic acid.

Anal. Calcd. for $C_9H_{13}Br_2NO$: Br (ionizable), 25.71. Found: Br, 25.69.

1-Fluoro-2,4-dimethyl-5-methoxy-6-bromobenzene.—A solution was made of 31.1 g. (0.1 mole) of the 1-amino-2,4-dimethyl-5-methoxy-5-bromobenzene hydrobromide in 10 cc. of concentrated hydrochloric acid and 25 cc. of water. The mixture was cooled to 0–5° and diazotized slowly with 6.9 g. of sodium nitrite in 15 cc. of water. After being allowed to stand for fifteen minutes, the solution was filtered and 17–25 cc. of cold fluoboric acid solution was added. The diazonium fluoborate was precipitated, filtered off, and washed successively with 5 cc. of fluoboric acid solution, 10 cc. of ethyl alcohol and 10 cc. of ethyl ether. The dry salt weighed 23 g. (70%). It was a pale yellow solid, quite soluble in water and fairly stable when dry. The decomposition temperature was about 105°. The desired fluoro compound was obtained from this diazonium salt by dry distillation in a flask connected to a condenser and wash bottles. The flask was gently heated to start the decomposition. If the reaction became so rapid as to tend to build up an internal pressure, the flask was externally cooled with tap water. After the diazonium salt was decomposed, the fluoro compound remaining in the flask was distilled under reduced pressure. The product weighed 12.2 g. (52%) based on the original amine hydrobromide. 1-Fluoro-2,4-dimethyl-5-methoxy-6-bromobenzene is a heavy colorless liquid of faint odor; b. p. 125° at 15 mm., n_D^{20} 1.5302, d_{20}^{20} 1.4350.

Anal. (Parr bomb). Calcd. for $C_9H_{10}BrFO$: Br, 34.3. Found: Br, 33.9.

Attempts to nitrate the molecule and replace the last vacant position were unsuccessful.

The Ullmann reaction with copper or zinc was unsatisfactory and the Grignard reagent could not be formed.

With aluminum chloride and acetic anhydride in carbon disulfide no reaction took place at low temperature, but heated to the boiling point of the reaction mixture, 1-fluoro-2,4-dimethyl-5-acetoxy-6-bromobenzene (described below) was formed.

1-Fluoro-2,4-dimethyl-5-nitrobenzene.—To 135 cc. of cold concentrated sulfuric acid 24.2 g. (0.2 mole) of 1-amino-2,4-dimethylbenzene was slowly added. The mixture was stirred until all of the amine sulfate dissolved and it was then cooled to 0–10° and 20 g. or 14.5 cc. (10% excess) of nitric acid (sp. gr. 1.42) was added. After standing for fifteen minutes, the solution was diluted with 400 g. of ice. The nitrated 1-amino-2,4-dimethylbenzene sulfate[9] precipitated but was not isolated.

The suspension was immediately diazotized by the addition of 13.8 g. of sodium nitrite in 30 cc. of water. After the diazotization mixture had stood for fifteen minutes,

[8] Boyce, Rankine and Robertson, *J. Chem. Soc.*, 1216 (1930).

[9] Nölting and Collin, *Ber.*, **17**, 265 (1884).

34–40 cc. of cold fluoboric acid was added. The precipitated diazonium fluoborate was filtered off, washed with ethyl alcohol and ether and dried. The weight was 28.2 g. (53% based on 1-amino-2,4-dimethylbenzene used). The dry diazonium fluoborate was quite stable; its decomposition temperature was 130°.

The salt was placed in a distilling flask connected to a condenser and wash bottles and decomposed as described for the other fluoborates. The product boiled at 133° at 30 mm.; 234° at 750 mm. The yield was 9.5 g. (53% based on the diazonium salt). The 1-fluoro-2,4-dimethyl-5-nitrobenzene was a pale yellow, heavy liquid; d_{20}^{20} 1.230, n_D^{20} 1.532.

Anal. (Micro). Calcd. for $C_8H_8FNO_2$: N, 8.28. Found: N, 8.10.

1-Fluoro-2,4-dimethyl-5-aminobenzene.—A mixture of 17.0 g. (0.1 mole) of 1-fluoro-2,4-dimethyl-5-aminobenzene, 25 g. of iron powder, 25 cc. of water and 5 cc. of dilute hydrochloric acid was placed in a 500-cc. flask fitted with a reflux condenser, and heated with shaking until the water refluxed from the heat of reaction. The reduction was completed by heating on the steam-bath for an hour, with the occasional addition of 1–2 cc. of dilute hydrochloric acid. The contents of the flask were neutralized with a few cubic centimeters of 20% sodium hydroxide solution and the 1-fluoro-2,4-dimethyl-5-aminobenzene steam distilled. The product separated from the steam distillate in white plates which turned pink or brown on contact with the air. It was purified by recrystallization from petroleum ether and then sublimation to give white plates melting at 57–58° (acetyl derivative from dilute alcohol, m. p. 133–134°).

Anal. (Micro). Calcd. for $C_8H_{10}FN$: N, 10.07. Found: N, 9.74.

1-Fluoro-2,4-dimethyl-5-amino-6-bromobenzene.—By addition of one mole equivalent of bromine to an acetic acid solution of 1-fluoro-2,4-dimethyl-5-aminobenzene, the hydrobromide of the 1-fluoro-2,4-dimethyl-5-amino-6-bromobenzene separated. The salt was readily recrystallized from glacial acetic acid. It decomposed without melting at 220°. The free base was purified by recrystallization from methyl alcohol and was obtained in white crystals melting at 56° (acetyl derivative from dilute alcohol, m. p. 170–171°).

Anal. (Volhard). Hydrobromide salt: Calcd. for $C_8H_{10}Br_2FN$: Br (ionized), 26.74. Found: Br, 26.85.

Nitration of 1-Fluoro-2,4-dimethyl-5-aminobenzene: 1-Fluoro-2,4-dimethyl-5-amino-3-nitrobenzene and 1-Fluoro-2,4-dimethyl-5-amino-6-nitrobenzene.—When 1-fluoro-2,4-dimethyl-5-aminobenzene was nitrated in concentrated sulfuric acid, two products were obtained. These were separated by their difference in solubility in petroleum ether. The less soluble nitration product, which was formed in smaller amounts, could be recrystallized from petroleum ether to give orange red crystals which melted at 88–89° (acetyl derivative from alcohol, m. p. 148–149°). This was identified by bromination in acetic acid to give 1-fluoro-2,4-dimethyl-3-nitro-5-amino-6-bromobenzene which was identical (m. p. 106°) with the product prepared by brominating first and then nitrating, as described in the next paragraph.

Anal. Calcd. for $C_8H_9FN_2O_2$: N, 15.2. Found: N, 15.29.

The more soluble part was recrystallized several times from petroleum ether to give a dark red compound melting at 72–74° (acetyl derivative from alcohol, m. p. 193–194°). Analysis of the amine indicated that it was an isomeric mononitro derivative, 1-fluoro-2,4-dimethyl-5-amino-6-nitrobenzene.

Anal. Calcd. for $C_8H_9FN_2O_2$: N, 15.2. Found: N, 14.76. The analysis of the acetyl derivative, which could be obtained in a purer form, confirmed this formula.

Anal. Calcd. for $C_{10}H_{11}FN_2O_3$: N, 12.38. Found: N, 12.34.

1-Fluoro-2,4-dimethyl-3-nitro-5-amino-6-bromobenzene.—To a solution of 10.9 g. (0.05 mole) of 1-fluoro-2,4-dimethyl-5-amino-6-bromobenzene in 25 cc. of cold concentrated sulfuric acid was added 1.4 cc. of nitric acid (sp. gr. 1.42) in 25 cc. of concentrated sulfuric acid. After standing for thirty minutes in the cold, the nitration mixture was poured onto 150 g. of cracked ice. The free amine precipitated, and was purified by recrystallization from petroleum ether giving a bright yellow solid, m. p. 105.5–106°.

Anal. (Micro). Calcd. for $C_8H_8BrFN_2O_2$: N, 10.65. Found: N, 10.72.

The attempts to replace the amino groups through the diazonium salt by hydroxyl or methoxyl were unsuccessful, though a chlorine could thus be introduced readily.

1-Fluoro-2,4-dimethyl-3-nitro-5-chloro-6-bromobenzene.—A solution of 1.3 g. (0.005 mole) of 1-fluoro-2,4-dimethyl-3-nitro-5-amino-6-bromobenzene in 12 cc. of cold hydrochloric acid was diazotized with 0.35 g. of sodium nitrite in 5 cc. of water. A solution of cuprous chloride in concentrated hydrochloric acid was then added and the 1-fluoro-2,4-dimethyl-3-nitro-5-chloro-6-bromobenzene precipitated. By purification from ethyl alcohol, white crystals were obtained, m. p. 113.5–114°.

Anal. (Parr bomb). Calcd. for $C_8H_6BrClFNO_2$: Cl + Br, 40.85. Found: Cl + Br, 40.7.

1-Fluoro-2,4-dimethyl-5-hydroxybenzene.—A solution of 2.8 g. (0.02 mole) of 1-fluoro-2,4-dimethyl-5-aminobenzene in 6 cc. of concentrated sulfuric acid and 12 g. of ice was diazotized with 1.4 g. of sodium nitrite in 6 cc. of water. The diazonium salt was decomposed to the phenol by dropping its solution slowly into a boiling mixture of 10 cc. of concentrated sulfuric acid and 7 cc. of water. The 1-fluoro-2,4-dimethyl-5-hydroxybenzene was steam distilled and extracted from the distillate with ethyl ether. The yield was 2.4 g. (85%). The phenol was purified by sublimation to give a white solid melting at 44–45°.

Anal. Calcd. for C_8H_9FO: C, 68.54; H, 6.48. Found: C, 68.41; H, 6.44.

1-Fluoro-2,4-dimethyl-5-hydroxy-6-bromobenzene.—The product was obtained by bromination of 1-fluoro-2,4-dimethyl-5-hydroxybenzene in glacial acetic acid. The product obtained by dilution of the reaction mixture was recrystallized from ethyl alcohol, m. p. 65–68°. This product was identical with that obtained by demethylation and simultaneous acetylation of the corresponding methyl ether previously described. It was purified from 50% ethyl alcohol, m. p. 75–76°.

Anal. (Micro) of the phenol and the acetyl derivative. Calcd. for C_8H_8BrFO: Br, 36.5. Found: Br, 36.7. Calcd. for $C_{10}H_{10}BrFO_2$: Br, 30.6. Found: Br, 30.8.

An attempt to nitrate the 1-fluoro-2,4-dimethyl-5-hydroxy-6-bromobenzene was unsuccessful.

Summary

1. 2,2′-Difluoro-3,3′-dicarboxy-6,6′-dimethoxydiphenyl has been synthesized. 1-Fluoro-2-iodo-3-methoxybenzene was condensed with copper to 2,2′-difluoro-6,6′-dimethoxydiphenyl. By means of acetyl chloride and aluminum chloride, 2,2′-difluoro-3,3′-diaceto-6,6′-dimethyldiphenyl was produced and this substance oxidized by sodium hypochlorite to 2,2′-difluoro-3,3′-dicarboxy-6,6′-dimethoxydiphenyl.

2. The alkaloidal salts showed no mutarotation. Only one form could be obtained of each and no active acids could be obtained by decomposition.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A STUDY OF SOME PARA-ALKYLPHENOLSULFONIC ACIDS

BY C. M. SUTER AND EUGENE W. MOFFETT

RECEIVED MARCH 19, 1932 PUBLISHED JULY 6, 1932

The purpose of this investigation was to prepare some sodium *p*-alkylphenolsulfonates and to determine their activity as antiseptics. It was thought that the presence of a sulfo group would confer the properties of increased solubility and decreased toxicity upon a phenol without seriously diminishing its bactericidal power. Since phenol-*o*-sulfonic acid has been shown[1] to be more active than its isomers and *p*-cresol-*o*-sulfonic acid more effective than phenol-*o*-sulfonic acid, it seemed reasonable to assume that the higher *p*-alkylphenol-*o*-sulfonic acids would be the most useful compounds of this type.

The four *p*-alkylphenols, *n*-propyl- to *n*-hexyl-, were sulfonated and the solubilities in water of the sodium salts of the resulting *o*-sulfonic acids were determined. The values obtained are listed in column four of Table I. It is interesting to note the alternation in the solubilities with the increase in the length of the alkyl group.

Determination of the phenol coefficients[2] indicated that only the *n*-propyl and *n*-butyl compounds have a detectable disinfectant action, the values for these being 1.8 and 2.4, respectively. A saturated solution of each of the other sulfonates gave no indication of bactericidal activity.

Experimental

***p*-Alkylphenols.**—These were made by a recently[3] used procedure involving the Fries reaction for the preparation of the *p*-hydroxyphenyl alkyl ketones and their reduction by the Clemmensen method to the alkylphenols. Part of the necessary phenyl esters were made from acyl chlorides and phenol and part of them by a method similar to one recently[4] reported.

Sodium *p*-Alkylphenol Sulfonates.—The sulfonation of *p*-butylphenol is described here. The other preparations were carried out in a similar manner.

A mixture of 40 g. of *p*-butylphenol and 30 cc. of concentrated sulfuric acid was heated on the steam-bath for an hour and poured into a saturated solution of sodium

TABLE I

Sodium *p*-phenol-*o*-sulfonate	Yield, %	S, % calcd.	S, % found	Sol. in H_2O at 26°, g./100 cc.	M. p. of *p*-toluidine salt, °C.
n-Propyl	56	13.44	13.47	1.52–1.61	141–143
n-Butyl	66	12.70	12.80	0.99–1.01	149–150
n-Amyl	72	12.04	11.90	1.30	147–149
n-Hexyl	83	11.43	11.45	0.54–0.48	139–140

[1] Frankel, "Arzneimittelsynthese," 6th ed., Julius Springer, Berlin, 1927, p. 542.

[2] We are indebted to Professors A. A. Day and A. W. Walker of the Department of Bacteriology of the Northwestern University Medical School for these determinations.

[3] Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

[4] Hartung, Munch, Miller and Crossley, THIS JOURNAL, **53**, 4153 (1931).

chloride. The precipitate of the sodium salt was twice recrystallized from hot water. The yield of pure product was 44 g. or 66% of the theoretical. The analytical data and yields of the four sulfonates are included in Table I.

The sulfur analyses were made by the Parr bomb method. The solubility determinations consisted of weighing the residues obtained by evaporation of the water from 25-cc. portions of saturated solutions of the various salts.

Summary

Four new *p*-alkylphenol-*o*-sulfonic acids have been made and the solubilities of their sodium salts in water determined. Of the compounds studied only the *n*-propyl- and *n*-butylphenolsulfonates have a measurable antiseptic action.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE MCCARTHY NEUROLOGICAL FOUNDATION AND THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, MEDICAL SCHOOL, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, AND THE LABORATORY OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE, ST. LOUIS]

THE MECHANISM OF THE PRODUCTION OF THIOL ACIDS (R SH) AND SULFONIC ACIDS (R SO_3H) FROM DITHIO ACIDS (R S S R). III. THE ACTION OF COPPER SALTS[1,2]

BY PAUL W. PREISLER AND DORIS B. PREISLER

RECEIVED MARCH 21, 1932 PUBLISHED JULY 6, 1932

Dithio acids (R S S R) have been shown to be simultaneously converted into thiol acids (R SH) and sulfonic acids (R SO_3H) by the action of Ag^+,[3,4] $BrHg^+$,[5] and Hg^{++},[6,7] the final result may be expressed by the equation

$$3R\,S\,S\,R + 3H_2O = 5R\,SH + R\,SO_3H$$

in which the formation of R SH and R SO_3H appears to be accelerated by reactants which remove the R SH by precipitation (Ag^+, Hg^{++}) or by formation of un-ionized complexes ($BrHg^+$).

The reaction between cupric salts and dithio acids has been studied by a quantitative method in which the corresponding sulfonic acid barium salt and the di-cuprous derivative of the thiol acid were isolated and identified. Of several possible reactions, the most probable is expressed by the equation

[1] Presented at the Meeting of the American Chemical Society in Buffalo, N. Y., September, 1931.

[2] The authors are indebted to the Smith, Kline and French Co., of Philadelphia, and to the Science Research Fund of Washington University, who have shared the expenses of this investigation with the respective institutions.

[3] Vickery and Leavenworth, *J. Biol. Chem.*, **86**, 129 (1930).

[4] Preisler and Preisler, *ibid.*, **89**, 631 (1930).

[5] Preisler and Preisler, *ibid.*, **95**, 181 (1932).

[6] Andrews and Wyman, *ibid.*, **87**, 427 (1930).

[7] Simonsen, *ibid.*, **94**, 323 (1931).

$$4HOOCCH_2CH_2SSCH_2CH_2COOH + 9H_2O + 10CuSO_4 = 5CuOOCCH_2CH_2SCu + 3HOOCCH_2CH_2SO_3H + 10H_2SO_4$$

This presents an interesting example of oxidation and reduction in which two substances in higher states of oxidation are both reduced at the expense of a further oxidation of part of one of the reactants. Reactions of this kind may be the cause of lower yields when copper salts are used in the isolation of R SH and R S S R compounds.

Experimental

Because of the ease of the isolation of the products, dithiodihydracrylic acid was selected for study of the reaction of dithio acids with copper sulfate and copper perchlorate. The quantity of di-cuprous compound that was isolated depended upon the acidity, the temperature, the concentrations and the presence of oxygen. Conditions were adjusted so as to obtain a high yield of products, since complete reaction apparently did not take place within reasonable time under the conditions studied. The maximum yield obtained was approximately 57% of the original dithio acid as a di-cuprous derivative.

Isolation of the Di-cuprous Thiol Derivative.—($CuSO_4$ reaction): 100 cc. of 0.2 *M* $CuSO_4$, 0.0025 *N* in H_2SO_4, and 325 cc. of water were placed in a flask fitted with a reflux condenser and heated in a boiling water-bath. Nitrogen, purified by passing over hot copper, was continuously passed through the solution to remove oxygen.

Fifty cc. of 0.1000 *N* di-sodium dithiodihydracrylate was added and the mixture heated for five hours. The light yellow precipitate was filtered off on a sintered glass crucible, washed with water containing a little sulfuric acid and then with acetone; amount of precipitate isolated (average of six experiments), 0.661 g., representing 57% of the original dithiodihydracrylic acid.

Analysis of the Di-cuprous Derivative.—Thiol determination: 0.30 to 0.45 g. of the precipitate was dissolved in excess potassium iodide and hydrochloric acid and titrated[2] with 0.1000 *N* potassium iodate: found, SH (average of six experiments), 14.26%; theoretical, 14.30%.

Copper determination: A 0.15 to 0.20 g. sample was dissolved in bromine water. After the removal of the excess of bromine by evaporation on the steam-bath, 3 g. of potassium iodide was added and the solution titrated with 0.1000 *N* sodium thiosulfate; found, Cu (average of six experiments), 54.3%; theoretical, 55.0%.

Isolation of the Di-cuprous Thiol Derivative.—($Cu(ClO_4)_2$ reaction): Sulfonic acid could not be isolated successfully from the sulfate solutions so similar experiments were carried out with perchlorate solutions: 150 cc. of 0.1 *M* copper perchlorate, 0.01 *N* in perchloric acid and 300 cc. of water were heated in a boiling water-bath, nitrogen was passed through, and 40.00 cc. of 0.1000 *N* di-sodium dithiodihydracrylate was added. The mixture was allowed to react for eight hours, after which the precipitate was filtered off. Amount of precipitate obtained (average of six experiments), 0.439 g., representing 47% of the original dithiodihydracrylic acid. To establish the identity of the compound, analyses for copper content, using 0.17 to 0.23 g. samples, were made: found (average of six experiments), 54.9%; theoretical, 55.0%.

Isolation of the Barium Salt of the Sulfonic Acid.—To the filtrate from the di-cuprous thiol compound was added 15 cc. of *N* barium perchlorate and then the mixture was saturated with hydrogen sulfide. After warming to coagulate, the copper sulfide (and a little barium sulfate) was filtered off and the filtrate was evaporated to about 10 cc. on the steam-bath. The solution was neutralized with *N* sodium hydroxide and one drop excess *N* perchloric acid was added; the white or gray precipitate which

formed was removed by centrifugalization. This precipitate is, perhaps, due to a decomposition of the dithiodihydracrylic acid present, since this gives a similar precipitate and a small amount of sulfonic acid when treated in a like manner. The solution and washings were evaporated to 50 cc., 150 cc. of 95% ethyl alcohol was added and the mixture warmed, whereupon precipitation of the barium sulfonate took place. This concentration of alcohol prevents the precipitation of the barium salt of the dithio acid. The mixture was cooled to about 7° and the crystalline precipitate filtered off on a sintered glass crucible. Isolated (average of five experiments) 0.284 g. of anhydrous $Ba(OOCCH_2CH_2SO_3)$, representing approximately 24.5% of the original dithio acid.

Analysis of the Barium Sulfonate.—A 0.1 to 0.18 g. sample of the precipitate was placed in a platinum dish and dried at 180° to obtain the anhydrous salt and then quickly weighed. The material was ignited in a muffle, treated with a few drops of sulfuric acid and again ignited. Found, Ba (average of five experiments), 46.8%. Theoretical, 47.5%.

ANALYTICAL DATA AND PRODUCTS OF THE REACTION BETWEEN DITHIODIHYDRACRYLIC ACID AND CUPRIC SALTS

Reaction with $CuSO_4$			Reaction with $Cu(ClO_4)_2$			
$CuOOCCH_2CH_2SCu$			$CuOOCCH_2CH_2SCu$		$Ba(OOCCH_2CH_2SO_3)$	
Isolated, g.	Cu, %	—SH, %	Isolated, g.	Cu, %	Isolated, g.	Ba, %
0.6679	54.6	14.18	0.4495	55.3	0.2820	47.2
.6598	54.3	14.30	.4338	54.7	.2706	46.7
.6574	54.4	14.35	.4363	54.9	.2888	46.7
.6566	54.2	14.26	.4371	54.5	.2959	46.7
.6559	54.1	14.16	.4408	55.0	.2849	46.5
.6678	54.3	14.33	.4374	54.8		
Av. 0.661	54.3	14.26	0.439	54.9	0.284	46.8
Calcd.	55.0	14.30		55.0		47.5

Discussion

The action of copper salts in causing the formation of sulfonic acids and thiol acids from dithio acids is probably due to reduction of the Cu^{++} to Cu^{+} with subsequent precipitation of the di-cuprous derivative. The reduction of Cu^{++} may result from the reaction with the R SH formed when water reacts with the dithio acid according to

$$3R\,S\,S\,R + 3H_2O = 5R\,SH + RSO_3H$$

Cupric ion is then reduced as follows

$$2R\,SH + 2Cu^{++} = R\,S\,S\,R + 2Cu^{+} + 2H^{+}$$

Cuprous ion then reacts with the R SH present forming the insoluble di-cuprous derivative similar to the reaction with Ag^{+},[4].

$$3HOOCCH_2CH_2SSCH_2CH_2COOH + 3H_2O + 5Cu_2SO_4 = 5CuOOCCH_2CH_2SCu + HOOCCH_2CH_2SO_3H + 5H_2SO_4$$

The sum of the properly substituted equations gives

$$4HOOCCH_2CH_2SSCH_2CH_2COOH + 9H_2O + 10CuSO_4 = 5CuOOCCH_2CH_2SCu + 3HOOCCH_2CH_2SO_3H + 10H_2SO_4$$

This series of reactions would require the conversion of 37.5% of the original dithio acid into sulfonic acid or a sulfonic acid—thiol derivative ratio of 0.60. The ratio calculated from the best experimental values is

0.52 and indicates that some Cu^{++} reduction is perhaps caused by material other than the —SH of the R SH.

The possibility of the occurrence of this series of reactions or any of its steps must be considered when isolating (as from biological material) R SH compounds (in the presence of oxidizing agents) or R S S R by means of cupric or cuprous salts, since sulfonic acids may result which cannot be easily reconverted into the original acids. Such reactions may also take part in the oxidation of R SH and R S S R when copper salts are used as catalysts.

The reaction is of chemical interest as an example of the interaction of two substances in higher states of oxidation to produce more reactive reducing substances and some of a more fully oxidized, unreactive product. The mechanism will be more fully discussed in a subsequent publication on the production of R SO_3H from R S S R by oxidizing agents.

St. Louis, Missouri

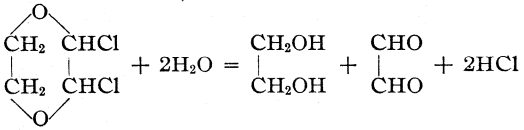
[Contribution from the Department of Research in Pure Chemistry, Mellon Institute of Industrial Research]

THE PREPARATION OF DI- AND ISOMERIC TETRACHLORODIOXANES

By C. L. Butler and Leonard H. Cretcher

Received March 23, 1932 Published July 6, 1932

Dichlorodioxane was recently prepared by Böeseken, Tellegen and Henriques[1] for use as an intermediate in the preparation of stereoisomeric 1,4,5,8-naphthodioxanes. A convenient means of determining the structure of the dichloro derivative was found in the easy hydrolysis of the substance in boiling water. As the aqueous solution of the hydrolysis product yielded quantitatively one molecular equivalent of glyoxal-*p*-nitrophenylosazone on treatment with *p*-nitrophenylhydrazine, it was concluded that the chlorine atoms were in vicinal positions. The hydrolysis apparently proceeded according to equation I. In the present paper, this work was confirmed and the evidence in support of equation I



(I)

was completed by the identification of glycol, as dibenzoate, among the hydrolysis products. As far as the present authors are aware, no other experiments on the chlorination of dioxane have been made. Van Alphen[2]

[1] Böeseken, Tellegen and Henriques, *Proc. Roy. Soc. Amsterdam*, **34**, 631 (1931); *Rec. trav. chim.*, **50**, 909 (1931).

[2] Van Alphen, *ibid.*, **49**, 1040 (1930).

attempted to brominate the substance by warming the bromine addition compound, $C_4H_8O_2Br_2$, but could isolate only ethylene bromide and aqueous hydrobromic acid from the reaction product.

Dioxane is now a commercial product, but its chemistry has been incompletely studied. It was thought by the present authors, therefore, that further investigation of its chlorinated derivatives would be of interest. The present paper consists of a report on the preparation and chemistry of dichloro- and of several isomeric tetrachlorodioxanes.

It is well known that glyoxal is a highly reactive substance and a useful reagent in many syntheses. As the usual method of preparation[3] is inconvenient, it appeared to be worth while to investigate the use in glyoxal condensations of solutions prepared by hydrolyzing dichlorodioxane. Employing this source of glyoxal, the *p*-nitrophenylosazone was prepared in quantitative yield by reaction with *p*-nitrophenylhydrazine; the diurea condensation product glycoluril,[4] was isolated in 70% yield; and from the latter hydantoin was prepared in 67% yield. Thus it is apparent that dichlorodioxane is a practical source of glyoxal for reactions of this type.

Dichlorodioxane.—This substance was prepared according to Böeseken, Tellegen and Henriques;[1] 208 g. of dioxane yielded 233 g. of pure dichlorodioxane boiling at 88–89° at 16–17 mm.; yield, allowing for 15 g. of recovered dioxane, 67.7%.

Glycol Dibenzoate.—1.6 g. of dichlorodioxane was decomposed by warming in 25 cc. of boiling water. A clear solution was obtained after about ten minutes' heating. The reaction mixture was cooled, made alkaline with sodium hydroxide and treated with benzoyl chloride in the usual way. The alkali-insoluble ester was extracted with ether and recrystallized from methyl alcohol. It melted at 70–72° on rapid heating.

Glyoxal-*p*-nitrophenylosazone.—1.6 g. of dichlorodioxane was decomposed as described above. An abundant red precipitate, which was formed on addition of an aqueous solution of 4 g. of *p*-nitropenylhydrazine hydrochloride to the cooled hydrolysis product, was filtered and washed with water and alcohol; yield, 3.2 g. of pure product melting at 306°, or 97% of the theoretical.

Glycoluril.—1.6 g. (1 mol) of dichlorodioxane was decomposed in 25 cc. of boiling water and the resulting acidic solution of glyoxal was mixed with an aqueous solution of 1.3 g. (2 mols) of urea. The mixture was warmed to the boiling point and then set aside. White crystals of glycoluril soon began to separate from the solution. After standing for several hours these were filtered, washed and dried. The yield was 1.0 g., or 70% of the theoretical; 15.6 g. of dichlorodioxane when treated similarly gave 8.7 g. of glycoluril, or 61.3% of the theoretical. The substance did not melt below 330°.

Hydantoin.—Nine grams of glycoluril was mixed with 36 g. of 25% hydrochloric acid and the mixture evaporated on a hot water bath until it weighed only 21 g.[3] Hydantoin crystallized from the solution on cooling in the ice box. A further quantity was obtained on evaporation of the mother liquor. The product was recrystallized from water. The yield of purified hydantoin melting at 214° was 4.3 g., or 67% of the theoretical.

---

[3] Siemonsen, *Ann.*, **333**, 111 (1904).

[4] Schiff, *ibid.*, **189**, 157 (1877); Bottinger, *Ber.*, **10**, 1923 (1877); Widman, *ibid.*, **19**, 2477 (1886); Biltz, *ibid.*, **40**, 4808 (1907); see also Pauly and Sauter, *ibid.*, **63B**, 2063 (1930).

The previous authors[1] also prepared diethoxydioxane by reaction of the dichloro compound with sodium ethylate. The method was improved in the present work by the substitution of absolute alcohol for sodium ethylate as reagent.

An attempted bromination gave the same negative results as were obtained by Van Alphen.[2]

Diethoxydioxane.—15.6 g. of dichlorodioxane was warmed on a water-bath for two and one-half hours with 30 cc. of absolute alcohol. Most of the hydrogen chloride and the excess of alcohol were removed by evaporation. The residue was taken up in ether, and the ether solution was washed with sodium bicarbonate solution and with water. The ether layer was dried with anhydrous sodium sulfate. The ether was evaporated off and the residue on distillation at 14 mm. gave 12.3 g. of diethoxydioxane boiling at 95–98°, or 71% of the theoretical yield.

Attempted Bromination of Dioxane.—Ninety grams of dioxane was kept gently refluxing and during six hours 335 g. of bromine was dropped into the liquid. The mixture was warmed for seven hours longer. On distillation of the reaction product 100 g. of liquid came over under 105°. The distillate collected in two layers, which were separated in a separatory funnel. The heavy layer was washed with water and dried with calcium chloride; 65.5 g. of ethylene dibromide boiling at 128–131° was obtained. The top layer consisted of aqueous hydrobromic acid. The residual tar could not be distilled.

2,3-Dichlorodioxane is theoretically capable of existence in *cis-* and *trans-* modifications. The facts that Böeseken, Tellegen and Henriques[1] were able to prepare stereoisomeric 1,4,5,8-naphthodioxanes and that chlorination of dioxane to the dichloro stage yields a uniform product, are interesting in this connection. Thus, although this substance is a constant boiling liquid, it may contain both of the possible isomers, because, on reaction with glycol, it yields two crystalline 1,4,5,8-naphthodioxanes.

The further chlorination of dioxane was next undertaken. It was hoped that the reaction would yield symmetrical tetrachlorodioxane, as this substance would give two molecular equivalents of glyoxal if its hydrolysis proceeded in a manner similar to the decomposition shown in equation I. However, the reaction product was found to consist of a mixture of tetrachlorodioxanes.

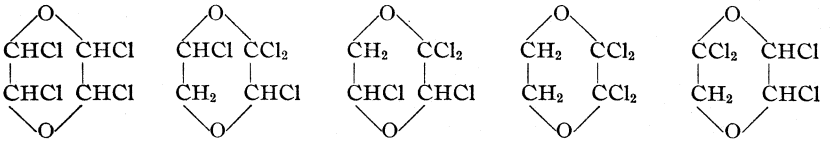
Preparation of Isomeric Tetrachlorodioxanes.—Two hundred grams of dioxane was chlorinated for twelve hours at 90°, as described previously.[1] Chlorine was then passed into the crude dichlorodioxane for twelve hours longer at 135–140°, heat being supplied by an oil-bath. Some crystalline material separated on cooling the reaction product. After standing for forty-eight hours in the ice box, the mixture was filtered, the crystals were set aside and the liquid was repeatedly fractionated at 11–12 mm.

As the distillations were continued, the top fractions yielded further small amounts of crystalline material. The lowest liquid fraction, 10 g. boiling below 90°, was not further investigated. The fractions between 95 and 100° also deposited crystals as the separation progressed, leaving a liquid fraction which on redistillation had a constant boiling point of 93–95°; yield, 57 g. The crystalline material from the low-boiling fractions was recrystallized from a mixture of ether and petroleum ether of boiling range 30–40°. The yield was 35 g. of white crystals melting at 57–58°. Several small

fractions (total weight 46 g.) of boiling point up to 120° were also obtained. The mixture of crystals from the crude reaction product and from the top fractions of the distilled liquid on recrystallization from ether yielded white needles melting at 143–144° in a yield of 22 g. and smaller flat crystals melting at 59–60°. The yield of the latter was 10 g.

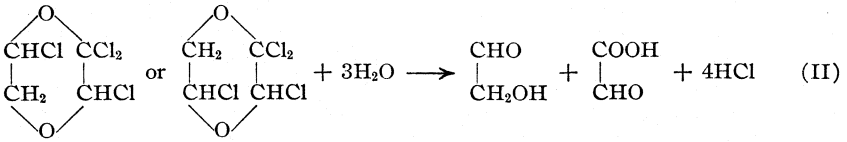
The four main fractions on analysis gave the correct value for tetrachlorodioxane. The structures of the compounds were determined by hydrolysis in boiling water and identification of the hydrolysis products in the form of their nitrophenylhydrazine derivatives.

Because the first stage of the chlorination was carried out under conditions which yield the known 2,3-dichlorodioxane, at least two of the chlorine atoms in the tetrasubstituted derivatives are in vicinal positions. The structural possibilities for the four compounds isolated are limited by this condition to those shown.



(a) (b) (c) (d) (e)

Tetrachlorodioxanes, b. p. 93–95° at 11–12 mm. and m. p. 57–58°, on decomposition with boiling water and subsequent treatment with *p*-nitrophenylhydrazine each yielded one molecular equivalent of glyoxylic acid *p*-nitrophenylhydrazone and one of glyoxal-*p*-nitrophenylosazone. The formation of glyoxylic acid on hydrolysis, together with the analytical data, indicates that these substances are tetrachlorodioxanes with three chlorine atoms on one side of the molecule and one on the other. They may be the structural isomers shown, formulas "b" and "c," or stereoisomers of either of these. The side of the molecule bearing the single chlorine atom should on hydrolysis yield glycolic aldehyde. The glyoxal-*p*-nitrophenylosazone obtained in the experiments is explained by the ease with which glycolic aldehyde is converted into this substance on treatment with *p*-nitrophenylhydrazine in acid solution.[5] The breakdown of these tetrachlorodioxanes is shown in Equation II.

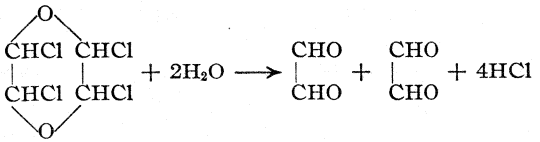


Formula "b" Formula "c"

Tetrachlorodioxanes, m. p. 59–60° and m. p. 143–144°, gave two molecular equivalents of glyoxal-*p*-nitrophenylosazone when solutions obtained by decomposing them with boiling water were treated with *p*-nitrophenyl-

[5] Wohl and Neuberg, *Ber.*, **33**, 3107 (1900).

hydrazine. They are therefore symmetrically substituted tetrachlorodioxanes and are two of five possible geometric isomers of formula "a." Their breakdown is shown in equation III.



Formula "a" (III)

Analyses of the Isomeric Tetrachlorodioxanes.—Calcd. for $C_4H_4O_2Cl_4$: Cl, 62.8. Found: liquid b. p. 93–95° at 11–12 mm., Cl, 62.1, d_4^{15} 1.5735; n^{25} 1.4956; crystals m. p. 57–58°, Cl, 63.1; crystals m. p. 59–60°, Cl, 63.1°, crystals m. p. 143–144°, Cl, 62.8.

Structure of the Isomeric Tetrachlorodioxanes.—Approximately 1.0-g. samples were heated under a reflux condenser with 50 cc. of water until clear solutions were obtained. The solutions were filtered and treated with 4.25 equivalents of *p*-nitrophenylhydrazine in dilute hydrochloric acid solution. A summary of the reaction products is shown in Table I.

TABLE I

Isomer	Sample, g.	Time of hydrolysis, hrs.	Products isolated	Calcd. yield, g.
Liquid b. p. 11–12 mm.	1.1	6	1.4 g. glyoxal *p*-nitrophenylosazone, m. p. 309°	1.6
			0.7 g. glyoxylic acid *p*-nitrophenylhydrazone[a]	1.0
Crystals, m. p. 57–58°	1.0	6	1.4 g. glyoxal-*p*-nitrophenylosazone, m. p. 306°	1.5
			0.6 g. glyoxylic acid *p*-nitrophenylhydrazone[a]	1.5
Crystals, m. p. 59–60°	1.0	2.5	2.8 g. glyoxal-*p*-nitrophenylosazone, m. p. 310°	2.9
Crystals, m. p. 143–144°	0.75	3	2.1 g. glyoxal-*p*-nitrophenylosazone, m. p. 310°	2.2

[a] This substance was identified by the facts that it darkened at about 180° and decomposed at about 200°,[6] and that it was soluble in dilute alkali to a beautiful deep red solution.

Formula "d" requires the formation of one molecule of oxalic acid and one of glycol, and formula "e" one of glycolic acid and one of glyoxal on hydrolysis. As neither of these sets of results agrees with the actual laboratory findings, these structures may be ruled out as applying to this work.

As a convenient source of glyoxal the tetrachlorodioxanes did not prove to be particularly suitable, mainly because of the low yields of symmetrically substituted compounds which give glyoxal on hydrolysis. All the compounds prepared had an odor resembling phosgene, which was more pronounced in the unsymmetrical tetrachloro derivatives. The liquid ap-

[6] Dakin and Dudley, *J. Biol. Chem.*, **15**, 136 (1913).

peared to be less stable than the other isomers, as it developed a strong odor of hydrochloric acid and lost about 3% of its chlorine on keeping for two weeks. The chlorine atoms in all these substances are quite reactive, and hence it is possible that further study will show interesting uses to which they might be put.

Some interesting information as to the relative stability toward hydrolysis of the di- and the isomeric tetra-substituted chloro derivatives of dioxane is available as a result of these studies. While dichlorodioxane is completely broken up by warming for ten or fifteen minutes in boiling water, two and one-half to three hours of heating were required to decompose the symmetrical tetrachloro derivatives which have quite similar structures. The unsymmetrical tetrachlorodioxanes were found to be even more stable, as five to six hours heating was required for their complete decomposition.

The yields of the various products obtained from 200 g. of dioxane are shown in Table II. That they are not higher is probably due in part to the many fractional distillations required to complete the separations.

TABLE II

	Grams
Material boiling under 90° at 11–12 mm., probably largely dichlorodioxane	10
Unsym.-tetrachlorodioxane, b. p. 93–95° at 11–12 mm.	57
Unsym.-tetrachlorodioxane, m. p. 57–58°	35
Sym.-tetrachlorodioxane, m. p. 59–60°	10
Sym.-tetrachlorodioxane, m. p. 143–144°	22
Total impure higher boiling fractions	46
Total	180

Summary

Dichloro- and tetrachlorodioxanes were prepared and studied as sources of glyoxal. Four of the many possible isomeric tetrachlorodioxanes were isolated and their structures determined.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

THE INTERACTION OF DIARYLARSYL IODIDES, DIARYLSTIBYL IODIDES AND PHENYLDIHALOARSINES WITH THE PIPERIDINE SALT OF N-PENTAMETHYLENE-DITHIOCARBAMIC ACID[1]

BY F. F. BLICKE AND U. O. OAKDALE[2]

RECEIVED APRIL 1, 1932 PUBLISHED JULY 6, 1932

N-Pentamethylene-S-triarylmethyldithiourethans are formed almost instantly and quantitatively from the interaction, at ordinary temperature, of a triarylmethyl halide and the piperidine salt of N-pentamethylenedithiocarbamic acid. These urethans are of interest because of the fact that they dissociate spontaneously, in solution, with the formation of triarylmethyls.[3]

$$R_3C{-}Cl + H{-}S{-}C(=S){-}NC_5H_{10}\cdot HNC_5H_{10} = R_3C{-}S{-}C(=S){-}NC_5H_{10} + C_5H_{10}NH\cdot HCl$$

$$R_3C{-}S{-}C(=S){-}NC_5H_{10} \longrightarrow R_3C{-} + {-}S{-}C(=S){-}NC_5H_{10}$$

In view of the great reactivity of the halogen in diarylarsyl and diarylstibyl iodides it seemed probable that these halides, too, might react with the piperidine salt of N-pentamethylenedithiocarbamic acid similarly to the triarylmethyl halides. It was found that piperidine hydriodide was precipitated almost immediately upon the addition of diphenylarsyl iodide, dissolved in benzene, to the piperidine salt of the dithiocarbamic acid. A colorless, crystalline compound was isolated from the benzene solution which, according to the results obtained from an analysis and molecular weight determination, was N-pentamethylene-S-diphenylarsyldithiourethan.

$$2\,(C_6H_5)_2As{-}I + 2\,H{-}S{-}C(=S){-}NC_5H_{10}\cdot HNC_5H_{10} = 2\,(C_6H_5)_2As{-}S{-}C(=S){-}NC_5H_{10} + 2\,C_5H_{10}NH\cdot HCl$$

$$(C_6H_5)_2As{-}As(C_6H_5)_2 \longleftarrow 2\,(C_6H_5)_2As{-} + 2\,{-}S{-}C(=S){-}NC_5H_{10}$$

Di-α-naphthylarsyl iodide, biphenylenearsyl iodide, 6-iodophenoxarsine, diphenylstibyl iodide and di-*p*-tolylstibyl iodide reacted with the piperidine salt in a manner entirely analogous to that described.

In the event that N-pentamethylene-S-diphenylarsyldithiourethan behaved similarly to the triarylmethyl analogs it should yield spontaneously, in solution, diphenylarsyl which would then polymerize, partly or com-

[1] This paper represents the second part of a dissertation to be submitted to the Graduate School by Mr. Oakdale in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Parke, Davis and Company Fellow.

[3] Blicke, THIS JOURNAL, **45**, 544 (1923).

pletely, to tetraphenyldiarsyl. This compound, as well as other tetraaryldiarsyls, absorbs with great rapidity an amount of oxygen which corresponds to that required for the formation of a peroxide.[4] Tetraphenyldistibyl reacts with oxygen in a similar manner.[5]

In one series of experiments the reactivity of the dithiourethans toward oxygen was tested by the use of the original reaction mixture. A number of sealed tubes were prepared; each tube contained the iodide, the required amount of the piperidine salt of N-pentamethylenedithiocarbamic acid and bromobenzene. After twenty-four hours the tubes were broken in an absorption apparatus and the contents exposed to oxygen, with continuous agitation, for two hours. No absorption of oxygen was noticed in any instance. Absorption experiments were repeated with the isolated dithiourethans with negative results.

Phenyldichloro- and phenyldi-iodoarsine react readily with two molecular equivalents of the piperidine salt of the dithiocarbamic acid from phenylarsylene N-pentamethylenedithiocarbamate, $C_6H_5As[S—C(=S)—NC_5H_{10}]_2$. Other alkyl- and aryldihaloarsines would, undoubtedly, react in an analogous manner. Many alkyl- and aryldihaloarsines are liquids or low melting solids, hence, it is difficult if not impossible to identify small amounts of these substances. No entirely satisfactory derivatives have been described hitherto which can be used for identification purposes; the dithiocarbamate, however, which can be obtained in sufficient amount from one drop of either of the above mentioned halides, seems to be especially suitable for this purpose because of the ease of its preparation,[6] the high molecular weight, sharp melting point and the low loss of material on recrystallization.

Experimental Part

N-Pentamethylene-S-diphenylarsyldithiourethan.—Two hundredths of a mole of diphenylarsyl iodide, dissolved in the smallest possible amount of warm benzene, was added to 0.02 mole of the piperidine salt of *n*-pentamethylenedithiocarbamic acid,[7] dissolved in warm benzene. Piperidine hydriodide precipitated immediately. The mixture was protected from moisture and after twelve hours the piperidine salt was removed by filtration and about 30 cc. of petroleum ether (30–60°) was added to the filtrate in order to precipitate a small quantity of piperidine hydriodide which had remained in solution. The hydriodide weighed 4.0 g.; the calculated amount is 4.2 g. To the benzene–petroleum ether solution there was added 150 cc. of petroleum ether whereupon the N-pentamethylene compound precipitated in crystalline form. The yield of the

[4] Blicke and Smith, THIS JOURNAL, **51**, 2272 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 780 (1930).

[5] Blicke and Oakdale, *ibid.*, **53**, 1025 (1931).

[6] In order to obtain the reagent it is merely necessary to add piperidine to a solution of carbon disulfide in absolute ether; the piperidine salt of the dithiourethan precipitates immediately.

[7] Cahours, *Ann. chim. phys.*, [3] **38**, 88 (1853); Ladenburg and Roth, *Ber.*, **17**, 514 (1884).

latter was 5.2 g. It was washed thoroughly with water to remove traces of piperidine hydriodide, dried and recrystallized from acetic acid or ethyl acetate.

Neither the original reaction mixture[8] nor the pure, isolated dithiourethan absorbed oxygen.

The molecular weight was determined in boiling benzene by the Menzies method. Calcd. mol. wt., 389; found, 386.

Dissolved in acetone the compound decolorized potassium permanganate, as well as iodine, instantly.

Diphenylchloroarsine was formed when the benzene solution of the compound was treated with hydrogen chloride at ordinary temperature.

A few drops of sulfuric acid were added to an acetic acid solution of the material and the mixture boiled for a few minutes. Diphenylarsinic acid was obtained as a reaction product.

Di-α-naphthylarsyl iodide, biphenylenearsyl iodide, 6-iodophenoxarsine, diphenylstibyl iodide and di-*p*-tolylstibyl iodide reacted in a similar manner with the piperidine salt of the dithiocarbamic acid.

TABLE I

DITHIOURETHANS

Iodide used in preparation	M. p., °C.	Formulas	As, Sb or Bi, % Calcd.	As, Sb or Bi, % Found	S, % Calcd.	S, % Found
Diphenylarsyl	114–115	$C_{18}H_{20}S_2NAs$	19.26	19.42	16.47	16.61
Di-α-naphthylarsyl[a]	214–215	$C_{26}H_{24}S_2NAs$	15.33	14.99	13.11	12.57
Biphenylenearsyl[b]	155–158	$C_{18}H_{18}S_2NAs$	19.36	19.31	16.56	16.39
6-Iodophenoxarsine[b]	105–106	$C_{18}H_{18}OS_2NAs$	18.59	18.50	15.90	15.51
Diphenylstibyl[c]	124–127	$C_{18}H_{20}S_2NSb$	27.92	27.77	14.70	14.54
Di-*p*-tolylstibyl[d]	123–124	$C_{20}H_{24}S_2NSb$	26.23	26.19	13.82	13.66

[a] Blicke and Smith, THIS JOURNAL, **51**, 1565 (1929).

[b] Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 781 (1930).

[c] Blicke, Oakdale and Smith, *ibid.*, **53**, 1026 (1931).

[d] The preparation of this iodide will be described in a later paper.

Phenylarsylene N-Pentamethylenedithiocarbamate, $C_6H_5As[S—C(=S)—NC_5H_{10}]_2$.—The following experiment illustrates the serviceability of the piperidine salt of the dithiocarbamic acid as a reagent for the identification of a very small quantity of phenyldi-iodoarsine. To one drop (0.0306 g.) of the latter compound there was added 0.127 g. (five times the calcd. amount), of the piperidine salt dissolved in about 3 cc. of dry benzene. The mixture was protected from moisture and after twelve hours the benzene was allowed to evaporate. The crystalline residue was washed with water until the piperidine hydriodide and excess piperidine salt of the dithiocarbamic acid had

[8] As a control experiment the reaction mixture obtained from 1.61 g. (0.005 mole) of triphenylmethyl bromide and 0.005 mole of the piperidine salt of the dithiocarbamic acid, dissolved in bromobenzene, was placed in the absorption apparatus and shaken vigorously. Previously, absorption experiments in the case of N-pentamethylene-S-triarylmethyldithiourethans had been carried out only with the isolated urethan. After one hour the reaction mixture had absorbed 60 cc. of oxygen and after two and one-half hours over 100 cc. had been absorbed. An absorption in excess of 56 cc., the required amount of gas for peroxide formation, is to be expected because of the union of the sulfur radical, formed during the dissociation of the dithiourethan, with oxygen. The formation of sulfur dioxide, or other volatile product, during the absorption naturally render the absorption procedure only a semi-quantitative one. Two-tenths of a gram of pure triphenylmethyl peroxide was isolated from the mixture.

been removed completely. The crude product weighed 0.022 g. One-half of the material was recrystallized from ethyl acetate; m. p. 173–174°.

Phenyldichloroarsine reacts in an analogous manner.

Anal. Calcd. for $C_{18}H_{25}S_4N_2As$: As, 15.87; S, 27.15. Found: As, 15.76; S, 26.92.

Summary

Diarylarsyl and diarylstibyl iodides react readily with the piperidine salt of N-pentamethylenedithiocarbamic acid to form N-pentamethylene-S-diarylarsyl- and N-pentamethylene-S-diarylstibyldithiourethans. Unlike the triarylmethyl analogs these substances do not undergo spontaneous decomposition in solution to form compounds of the type $R_2As—AsR_2$ and $R_2Sb—SbR_2$. Phenyldihaloarsines and the piperidine salt of the dithiourethan interact to yield a dithiocarbamate. Because of the advantageous properties of this substance the piperidine salt of the dithiocarbamic acid is suggested as a reagent for the identification of small quantities of alkyl- and aryldihaloarsines.

ANN ARBOR, MICHIGAN

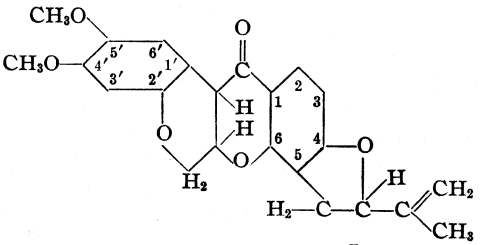
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. XXII. SOME NEW DATA IN CONFIRMATION OF THE STRUCTURE OF ROTENONE

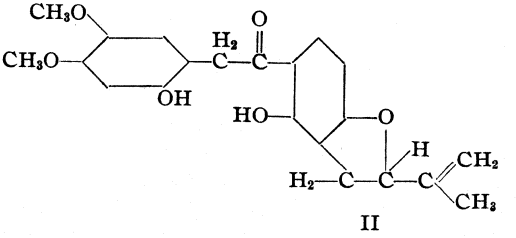
BY L. E. SMITH AND F. B. LAFORGE

RECEIVED APRIL 6, 1932 PUBLISHED JULY 6, 1932

The complete formula for rotenone having been established on the basis of its principal reactions as I,[1] reference should be made to several other typical reactions not explained in previous articles.



I

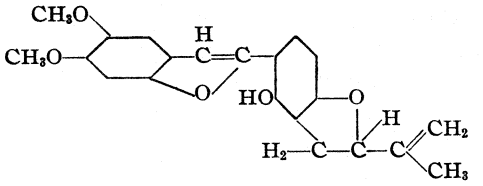


II

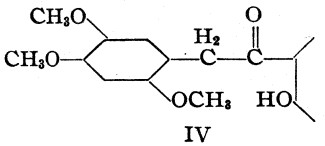
[1] LaForge and Haller, THIS JOURNAL, 54, 810 (1932).

Derritol has been shown to correspond to the formula II[1] and analogous structures apply to its derivatives, iso- and dihydroderritol.

The derritols are converted into anhydroderritols with loss of one molecule of water. The reaction mechanism proposed by Butenandt for this transformation has proved to be correct, and anhydroderritol therefore corresponds to the formula III.[2] The reaction is, however, best accomplished by boiling the compounds in xylene solution with phosphorus pentoxide rather than by distillation as recommended by Butenandt. The anhydroderritols all contain a free phenolic hydroxyl group in position 6 and can be acetylated to monoacetyl compounds which do not give the ferric chloride reaction. They are insoluble in alkali, a property which is in agreement with the fact that all phenols of the rotenone series with only one hydroxyl group in the 6 position, are alkali insoluble.[1]



III



IV

The methylderritols, IV, do not yield anhydrides although they give the color reaction with ferric chloride and are easily acetylated to compounds which do not give the test. It has already been observed that the derritols themselves give two moles of hydrogen by the Zerewitinoff method.[2]

All these relations serve as further confirmation of formula III for derritol.

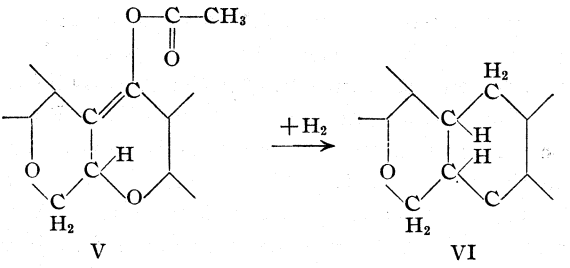
As previously reported, dehydrodihydrorotenonic acid is easily acetylated in position 4 to a monoacetyl compound. From analogy it could be predicted that dihydrorotenonic acid would yield a corresponding monoacetyl derivative. Contrary to expectations, however, treatment of dihydrorotenonic acid with acetic anhydride and sodium acetate resulted in the formation of a diacetyl derivative.

Rotenone, dihydrorotenone and isorotenone on treatment with acetic anhydride yielded monoacetyl compounds.

These results might have been very disturbing in the speculations on the structure of rotenone, had they been observed before the rotenone formula had been established. They are, however, easily explained on the assumption that rotenone and rotenonic acid react to form enol acetates, V. This theory has been proved definitely by the fact that on catalytic hydrogenation acetyldihydrorotenone is easily converted into dihydrodesoxyrotenone, VI, with simultaneous loss of the acetyl group.[3] The enol acetates

[2] Butenandt, *Ann.*, **464**, 253 (1929).

[3] Roll and Adams, THIS JOURNAL, **53**, 8469 (1931).



V VI

of rotenone and dihydrorotenone give promise of being of practical importance owing to their comparative stability toward oxidation. Comparative toxicity tests are being made on these compounds. The structure of rotenonone will be discussed in a future communication.

Experimental

The Anhydroderritols.—Two grams of substance was dissolved in 75 cc. of xylene and 4 g. of phosphorus pentoxide was added in small portions to the boiling solution. The solution was then decanted from the viscous residue and evaporated to dryness on the steam-bath. The crude product crystallized on cooling. The yield in all cases was about 1.5 g.

Anhydro-	Recrystallized from	M. p. °C.	Ferric chloride test	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Derritol	CH_3OH	160	Red	$C_{21}H_{20}O_5$	71.55	5.72	71.74	5.80
Isoderritol	CH_3OH	149	Red	$C_{21}H_{20}O_5$	71.55	5.72	71.79	5.72
Dihydroderritol	Dil. MeOH	164	None	$C_{21}H_{22}O_5$	71.18	6.21	71.04	6.39

The Acetylanhydroderritols.—One gram of substance, 0.2 g. of anhydrous sodium acetate and 10 cc. of acetic anhydride were refluxed for two hours. When the solution was poured into water the substance was obtained crystalline. The yield in all cases was about 1 g. Acetyldihydroderritol methyl ether was obtained by the same method.

No.		Recrystallized from	M. p., °C.	Ferric chloride test
1	Acetylanhydroderritol	CH_3OH	146	None
2	Acetylanhydroisoderritol	C_2H_5OH	158	None
3	Acetylanhydrodihydroderritol	C_2H_5OH	138	None
4	Acetyldihydroderritol methyl ether	C_2H_5OH	98	None

No.	Formula	Analyses, % Calcd. C	Calcd. H	CH_3CO	OCH_3	Found C	Found H	CH_3CO	OCH_3
2	$C_{23}H_{22}O_6$	70.05	5.58			70.07	5.51		
3	$C_{23}H_{24}O_6$	69.69	6.06			69.73	6.02		
4	$C_{24}H_{28}O_7$	67.28	6.54	10.04	21.72	67.33	6.64	10.41	21.71 21.46

Diacetyldihydrorotenonic Acid.—One gram of dihydrorotenonic acid, 0.3 g. of anhydrous sodium acetate and 16 cc. of acetic anhydride were refluxed for one hour, and the solution then evaporated to dryness on the steam-bath. The product was washed with water and then recrystallized from dilute ethyl alcohol. The substance melted at 115–116°. It was again recrystallized from petroleum ether (b. p. 80–100°) and it

then melted at 119°; yield, 0.8 g. Calcd. for $C_{27}H_{30}O_8$: C, 67.22; H, 6.22; $2CH_3O$, 12.86; $2CH_3CO$, 17.84. Found: C, 67.62, 67.23; H, 5.91, 6.15; CH_3O, 13.17, 12.87; CH_3CO, 17.79.

This same compound was obtained when 2 g. of dihydrorotenonic acid dissolved in 5 cc. of pyridine was treated in the cold with 1 g. of acetyl chloride. After standing at room temperature for three days, water was added and the mixture extracted with ether. The ether extract was extracted twice with water, twice with 10% hydrochloric acid and once with 10% potassium carbonate solution. After drying over anhydrous sodium sulfate the ether was evaporated and the product recrystallized from petroleum ether, m. p. 119°. When the substances obtained by the two methods were mixed, the melting point was not depressed.

The Acetylrotenones.—One gram of substance, 0.3 g. of anhydrous sodium acetate and 16 g. of acetic anhydride were refluxed for one hour, and the solution was then evaporated to dryness on the steam-bath. After washing with water the products were recrystallized. The compounds can also be prepared by the pyridine–acetyl chloride method as in the case of diacetyldihydrorotenonic acid. Acetylisorotenone is distinctly yellow in color whereas the corresponding rotenone and dihydrorotenone derivatives are only very slightly colored.

	Recrystallized from	M. p., °C.	Formula	Analyses Calcd. C	H	CH_3CO	OCH_3	Found C	H	CH_3CO	OCH_3
Acetyldihydrorotenone	C_2H_5OH	209–211	$C_{25}H_{26}O_7$	68.49	5.93	9.86	14.15	68.48	6.11	9.68	14.26
Acetylrotenone	C_2H_5OH	135	$C_{25}H_{24}O_7$	68.8	5.5		14.22	68.97	5.75		14.17
Acetylisorotenone	C_2H_5OH	144	$C_{25}H_{24}O_7$	68.8	5.5		14.22	68.75	5.58		14.22

Dihydrodesoxyrotenone from Acetyldihydrorotenone.—Four-tenths gram of acetyldihydrorotenone in acetic acid solution was reduced with hydrogen under 50 pounds pressure with 0.2 g. of platinum oxide catalyst. The substance crystallized when the acetic acid solution was diluted with water. It was filtered off, dissolved in ether, and the ether solution was extracted with 5% potassium hydroxide. The ether solution was then dried over anhydrous sodium sulfate and evaporated to dryness. The product was recrystallized from methyl alcohol; m. p. 168°, yield 0.3 g. When mixed with dihydrodesoxyrotenone there was no depression of melting point.

Anal.[4] Calcd. for $C_{23}H_{26}O_5$: C, 72.28; H, 6.86. Found: C, 72.23, 72.08; H, 6.97, 7.05.

Summary

Anhydroderritols were prepared from derritol, isoderritol and dihydroderritol by the action of phosphorus pentoxide on the xylene solution of the corresponding derritols.

The methylderritols do not yield anhydrides.

The anhydroderritols are alkali insoluble but give ferric chloride color reactions and can be acetylated.

The mechanism of the formation of the anhydroderritols proposed by Butenandt has proved to be correct. These reactions serve as a confirmation of the derritol formula as previously proposed. Dihydrorotenonic acid gives a diacetyl derivative. Rotenone, isorotenone and dihydrorotenone give monoacetyl compounds. These acetyl compounds belong to

[4] These analyses were made by Mr. J. R. Spies of this division.

the class of enol acetates and one of the acetyl groups in dihydrorotenonic acid is of this type.

Dihydrorotenone monoacetate is reduced by catalytic hydrogen to dihydrodesoxyrotenone.

WASHINGTON, D. C.

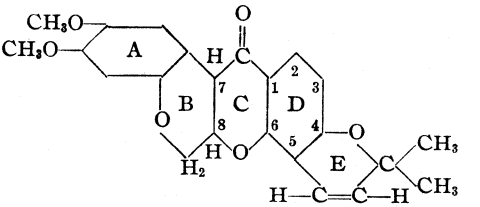
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

DEGUELIN. IV. THE STRUCTURE OF DEGUELIN AND TEPHROSIN

BY E. P. CLARK

RECEIVED MAY 3, 1932 PUBLISHED JULY 6, 1932

On the basis of information now available it may be stated with a considerable degree of assurance that the structure of deguelin is represented by formula I.



I. Deguelin, $C_{23}H_{22}O_6$

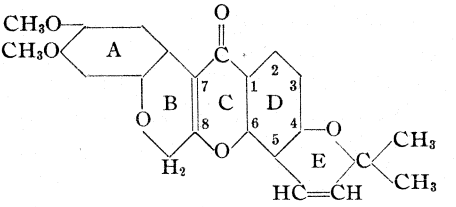
This statement is based upon facts concerning reactions of deguelin previously published together with certain new information which will be presented at this time and also upon the important observation previously made relative to relationships existing between deguelin and rotenone.

As the reactions principally involved in establishing that portion of the structure of deguelin represented by rings A, B, C and D have been recorded[1] and an interpretation of these reactions has been made in establishing the same structures in toxicarol,[2] it will be necessary only to refer to these facts briefly.

Deguelin, like rotenone and toxicarol, contains two hydrogen atoms which are readily removed by mild oxidation. In their place a double bond is introduced into the molecule, and the oxidation product, dehydrodeguelin (formula II), undergoes reactions which establish the fact that the position of the new double bond is between the carbon atoms common to rings B and C (designated in the formula as carbon atoms 7 and 8). The facts supporting the last statement are as follows: first, permanganate oxidation of dehydrodeguelin yields three products, namely, 2-hydroxy-4,5-dimethoxybenzoic acid, risic acid (2-carboxy-4,5-dimethoxyphenoxyacetic

[1] Clark, THIS JOURNAL, (a) **53**, 313 (1931); (b) **53**, 2369 (1931); (c) **53**, 3431 (1931); (d) **53**, 2007 (1931).

[2] Clark, *ibid.*, **54**, 2537 (1932).

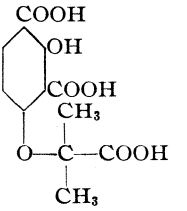


II. Dehydrodeguelin, $C_{23}H_{20}O_6$

acid) and a new tricarboxylic acid, $C_{12}H_{12}O_8$, which has been designated as nicouic acid. Second, hydrolysis of dehydrodeguelin with alcoholic potassium hydroxide yields deguelic acid, $C_{23}H_{24}O_8$, which upon oxidation with potassium permanganate gives risic acid. If, however, the oxidizing agent is alkaline hydrogen peroxide, derric acid (2-carboxymethyl-4,5-dimethoxyphenoxyacetic acid) is formed. Disregarding for the moment nicouic acid, the interpretation of these facts is the same as was presented in developing that portion of the structure of toxicarol which is identical with rings A, B and C in the deguelin formula presented above.[2] It follows, therefore, that deguelin, having no free hydroxyl as is the case with toxicarol, undoubtedly possesses the structure represented by rings A, B, C and D. There then remain only the elements C_5H_6O to be accounted for.

Available information concerning this grouping is purely of an analytical character, but the evidence is fairly conclusive that the structure represented by ring E in formulas I and II is correct.

Deguelin has been shown to be optically inactive[1a] and it also possesses a double bond capable of reduction to a dihydro derivative. Except for the configurations of carbon atoms 7 and 8 which are assumed to be racemized in the process of preparing deguelin, as was also suggested as being the case with toxicarol,[2] formula I satisfies the two conditions just mentioned. It has further been shown that permanganate oxidation of dehydrodeguelin yields besides 2-hydroxy-4,5-dimethoxybenzoic and risic acids, nicouic acid, to which reference was made above.



III. Nicouic acid, $C_{12}H_{12}O_8$

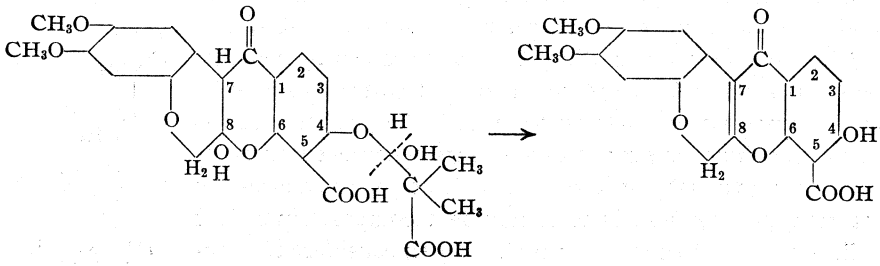
Nicouic acid is a tricarboxylic acid, as shown by combustion, titration and the methoxyl content of its methyl ester. It decomposes at its melting point with the evolution of gas and at the same time gives as one of its decomposition products α-hydroxyisobutyric acid. It also gives the fluorescein reaction for resorcinol,[3] and it may be decomposed in boiling aniline solution to give resorcinol. When considered in conjunction with the structure of that portion of the dehydrodeguelin molecule represented by rings A, B and C in formula II and also the manner in which permanganate attacks the molecule, these facts indicate that nicouic acid has the structure represented by III.

[3] Mulliken, "Identification of Pure Organic Compounds," 1905, Vol. I, p. 110.

Further evidence bearing upon the nature of ring E has been obtained through another source. It has been shown that tephrosin, $C_{23}H_{22}O_7$, is a hydroxydeguelin[4,5] and that the hydroxyl group replaces one of the easily oxidizable hydrogen atoms attached to carbon atoms 7 or 8 in deguelin. It has also been shown that tephrosin is oxidized by potassium permanganate to a dicarboxylic acid, $C_{23}H_{22}O_{11}$ (IV),[4] in which process the ring containing the double bond (ring D) is split and four atoms of oxygen are added. No loss of carbon or hydrogen occurs.

Tephrosin dicarboxylic acid, when dissolved in hot diphenyl ether and then heated a short time to the boiling point of the solvent, loses the elements $C_4H_8O_3$ and yields a phenolic monocarboxylic acid, $C_{19}H_{14}O_8$ (V), to which the name tephrosin monocarboxylic acid has been given. In this process the hydrogen atom and the hydroxyl group attached to carbon atoms 7 and 8 are removed as water with the generation of a double bond, so that tephrosin monocarboxylic acid belongs to the dehydro series of derivatives. This fact is shown not only by the insolubility of the product, a characteristic of dehydro derivatives of the rotenone group of fish poisons, but also because of its composition and its ability, when treated with alcholic potassium hydroxide solution, to undergo hydrolysis with the formation of a new carboxyl and phenolic hydroxyl group (deguelic or derrisic acid reaction).

The remaining portion of the $C_4H_8O_3$, namely, $C_4H_6O_2$, which is lost by tephrosin dicarboxylic acid, consists of α-hydroxyisobutyric acid. Evidence of this was obtained by isolating the α-hydroxyisobutyric acid as a decomposition product of the reaction. Because α-hydroxyisobutyric acid is removed from the original acid with the simultaneous generation of a hydroxyl group in ring D, demonstrated by a positive ferric chloride test and the formation of an acetyl derivative, it is obvious that the process is one of hydrolysis and may be represented as follows



IV. Tephrosin dicarboxylic acid, $C_{23}H_{22}O_{11}$

V. Tephrosin monocarboxylic acid, $C_{19}H_{14}O_8$

[4] Clark, THIS JOURNAL, **53**, 729 (1931).

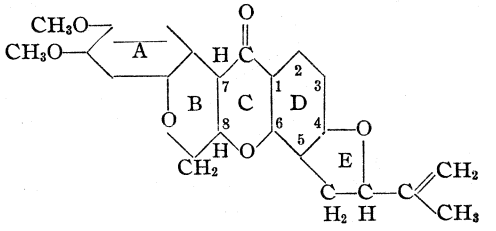
[5] Besides acetic anhydride or a mixture of acetic and sulfuric acids other dehydrating agents convert tephrosin into dehydrodeguelin. An acetyl derivative of tephrosin has also been prepared (see experimental part).

The reaction is important, however, aside from showing the nature of the C_4 group, in that tephrosin monocarboxylic acid undergoes the Dakin reaction, yielding risic acid, and therefore restricts the possible positions of the hydroxyl group in tephrosin monocarboxylic acid and consequently the oxygen linkage of ring E in deguelin and tephrosin. The Dakin reaction has been discussed recently in connection with its application to the structure of toxicarol,[2] and from that discussion it follows that the hydroxyl group in ring D of tephrosin monocarboxylic acid is either at position 2 or 4.

From the facts presented relative to nicouic and tephrosin dicarboxylic acids it follows that the grouping C_5H_6O in deguelin and tephrosin consists of an optically inactive unsaturated pyran ring, which can be represented only as indicated by ring E.

In the data thus far presented only two facts bear upon the attachment of ring E to ring D. This of course refers to the application of the Dakin reaction to tephrosin monocarboxylic acid and the evidence that nicouic acid is a resorcinol derivative. However, another approach to this problem is available as a result of the observation that dihydrodehydrodeguelin and dihydrodeguelic acid are respectively identical with dehydro-β-dihydrorotenone and dehydrodihydroxy-β-dihydrorotenonic acid.[1b]

It has recently been demonstrated by LaForge and Haller[6] that rotenone may be represented by formula VI, and in the course of this work it was



VI. Rotenone

shown that rotenonic acid is formed from rotenone by opening the furan ring (E) by hydrogenation.

Haller[7] also found that in attempting to isomerize rotenonic acid to isorotenonic acid with glacial acetic and sulfuric acids, ring closure occurred in a measure analogous to the formation of a saturated lactone from an unsaturated acid and yielded an alkali-insoluble compound which he designated as β-dihydrorotenone. Mild oxidation of this compound removed the readily oxidizable hydrogen atoms on carbon atoms 7 and 8 in formula VI and yielded dehydro-β-dihydrorotenone. Hydrolysis of the dehydro-β-dihydrorotenone with alcoholic alkali yielded what was called dehydrodi-

[6] LaForge and Haller, THIS JOURNAL, 54, 810 (1932).

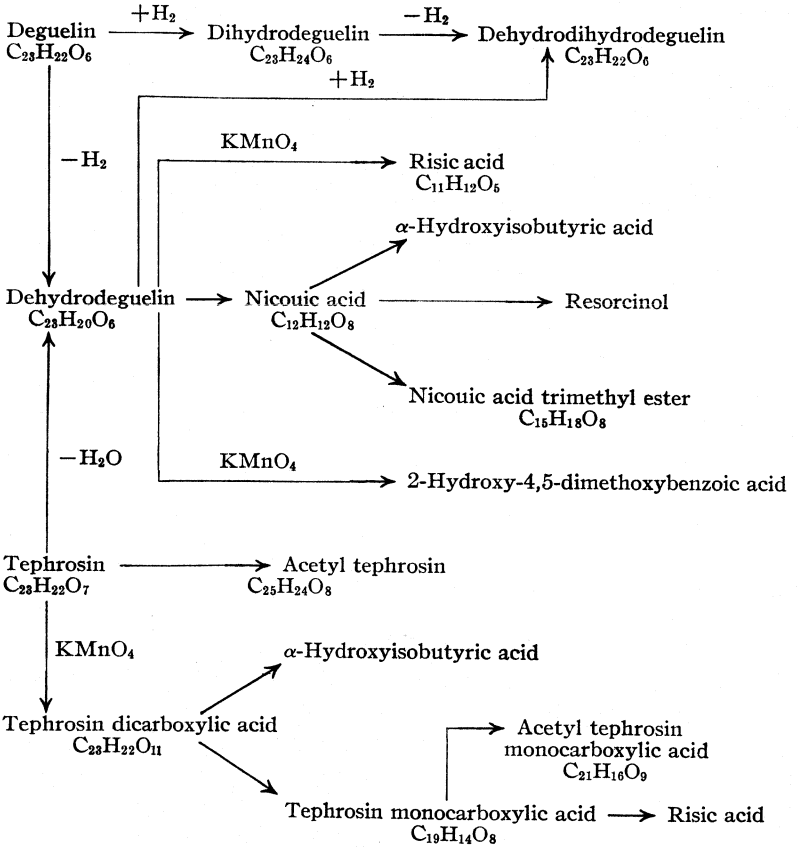
[7] Haller, *ibid.*, 53, 733 (1931).

hydroxy-β-dihydrorotenonic acid. These β-dihydrorotenone compounds, as stated before, were the same as dehydrodihydrodeguelin and dihydrodeguelic acid, respectively. From the way in which the β-dihydrorotenone derivatives were prepared it follows that no shift of points of attachment of ring E to ring D in rotenone occurred, and therefore ring E in deguelin and tephrosin is attached to ring D as indicated in formula I.

The relationships existing between the β-dihydrorotenone and deguelin derivatives are also verification of that portion of the structure of deguelin represented by rings A, B, C and D which was developed upon evidence relating to independent reactions of deguelin and its derivatives.

The reactions involved in the foregoing discussion which have been presented for the first time are summarized in the accompanying chart.

NEW REACTIONS OF DEGUELIN AND TEPHROSIN AND SOME OF THEIR DERIVATIVES



Experimental

Dihydrodeguelin.—A solution of 5 g. of deguelin in 150 cc. of hot acetic acid was reduced at atmospheric pressure and 75° with hydrogen and the platinum catalyst of

Voorhees and Adams.[8] The catalyst was removed, and the solution was concentrated *in vacuo* to a sirup, which was dissolved in 35 cc. of methanol and allowed to crystallize. Three and six-tenths grams of colorless crystals separated which melted at 153–155°. This material when recrystallized from various solvents gave products which appeared to be uniform but which did not melt sharply. The melting points of the various preparations also differed from each other over the range from 153° to 163°, and combustion analysis gave carbon and hydrogen results which, while uniform, were too high to warrant the assumption that the material was pure.

A portion of the reduced material dissolved in ethyl acetate was then treated for two hours with hydrogen and the platinum catalyst at a pressure of 375 pounds. The resulting product obtained as outlined above was recrystallized by dissolving it in the necessary quantity of chloroform and adding an excess of methanol. It melted sharply at 173–174° and gave satisfactory analysis.

Anal. Calcd. for $C_{23}H_{24}O_6$: C, 69.67; H, 6.10; OCH_3, 15.66. Found: C, 69.31; H, 6.08; OCH_3, 15.6.

To further identify the compound as dihydrodeguelin it was oxidized to dehydrodihydrodeguelin with potassium ferricyanide in the manner in which dehydrodeguelin was prepared from deguelin.[1a] The product was shown to be the material expected by comparison with an authentic sample of dehydrodihydrodeguelin.

Risic Acid by Permanganate Oxidation of Dehydrodeguelin.—The mother liquors from which the 2-hydroxy-4,5-dimethoxybenzoic acid was obtained by oxidizing 50 g. of dehydrodeguelin with permanganate[1c] were thoroughly extracted with ether. The extract was dried with sodium sulfate and concentrated to a volume of approximately 50 cc. As the operation proceeded a small quantity (150–160 mg.) of risic acid separated. It was purified according to the directions previously recorded[9] and then was shown to be pure risic acid by comparison with an authentic sample of this material.

Nicouic Acid.—After removing the risic acid from the above ether extract, the mother liquors were concentrated to a sirup and dissolved in 150 cc. of boiling chloroform. Upon standing, 8.2 g. of nicouic acid separated as groups of irregularly shaped salmon-colored rods and plates. Upon spontaneous evaporation the mother liquors left a mass of highly colored sticky crystals. These were dissolved in a large excess of boiling 5% potassium hydroxide solution and treated with small quantities of 30% hydrogen peroxide until the color of the liquid became light yellow. The solution was then acidified with sulfuric acid, filtered through norit and extracted with ether. The purified acid was recovered from the ethereal solution as outlined above. The yield was 2 g., making in all 10.2 g. of **nicouic acid** from 50 g. of dehydrodeguelin.

For analysis the acid was purified by treatment with hydrogen peroxide as outlined above and then recrystallized once from boiling chloroform. Thus obtained it consisted of colorless rods which melted at 196° with decomposition. They showed inclined extinction (crossed nicols), double refraction was extremely strong and only partial biaxial interference figures were shown in convergent polarized light; α, 1.455; β, indeterminate and $\gamma > 1.740$.[10]

It gave a wine red color with ferric chloride and when it was condensed with phthalic anhydride a yellow-green fluorescent solution (fluorescein) was obtained showing that the acid was a resorcinol derivative.[3]

Anal. Calcd. for $C_{12}H_{12}O_8$: mol. wt., 284.2; C, 50.69; H, 4.26. Found: mol. wt., titration calcd. as a tricarboxylic acid, 291; C, 50.23; H, 4.44.

[8] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

[9] Clark, *ibid.*, **54**, 1600 (1932).

[10] The optical data here recorded were determined by Geo. L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture.

Nicouic Acid Methyl Ester.—A solution of 1 g. of nicouic acid in 25 cc. of 5% methanolic hydrochloric acid solution was refluxed for two hours and then allowed to stand at room temperature overnight. The liquid was then poured into crushed ice, and after the ice had melted, the liquid was extracted with ether. The ethereal solution was thoroughly washed with water and then dried. The extract was freed from ether and dissolved in methanol and sufficient water was added to cause a slight turbidity. Crystallization soon began, yielding colorless plates which melted at about 90°. The yield was 280 mg. The material was recrystallized from dilute methanol until its melting point rose to 120–121°.

Anal. Calcd. for $C_{15}H_{18}O_8$: C, 55.20; H, 5.56; OCH_3 (3), 28.5. Found: C, 55.12; H, 5.81; OCH_3, 27.5.

α-Hydroxyisobutyric Acid from Nicouic Acid.—Approximately 0.1 g. of nicouic acid was carefully heated in a large test-tube until the material melted and the resultant effervescence subsided. The test-tube was then connected to a high vacuum, and the melt was subjected to distillation as long as any material condensed on the cool portion of the tube.

During the entire process of heating and distilling, a sublimate of long, beautiful crystals collected on the cool portion of the test-tube. This was α-hydroxyisobutyric acid. After purification by sublimation it melted at 79° and when mixed with an authentic sample of α-hydroxyisobutyric acid the melting point was not depressed.

Another product of the decomposition of nicouic acid by this treatment was a water-soluble acid which gave a deep blue color reaction with ferric chloride and melted at 162°. As this material has not been completely investigated it will not be reported upon at this time.

Resorcinol from Nicouic Acid.—A solution of 1 g. of nicouic acid in 4 cc. of aniline was heated to its boiling point and maintained at this temperature until gas was no longer evolved.

The resultant liquid was then mixed with 25 cc. of water, and the mixture was steam distilled until the aniline was completely removed. The residual aqueous solution was cooled in ice, filtered through a little norit, treated with approximately 2 g. of sodium bicarbonate and extracted with ether. The ethereal solution was dried, evaporated to dryness and dissolved in chloroform. After standing for some time the solution crystallized. The product was resorcinol, melting point 110°. The identification consisted of comparing the product with a known sample of resorcinol as to melting point, mixed melting point and optical properties, all of which were in agreement. The crystals were also nitrated according to the directions of Mulliken,[3] and the product was shown by comparison with an authentic sample to be trinitroresorcinol.

Acetyl Tephrosin.—A solution of 2 g. of tephrosin in a mixture of 12 cc. of pyridine and 12 cc. of acetic anhydride was allowed to stand at room temperature for two days. Two volumes of methanol were then added to the reaction mixture and, after the resulting liquid was cooled, water was added until a slight turbidity was produced. Crystallization began at once, and yielded 1.85 g. of acetyl tephrosin. Upon recrystallization from dilute methanol it melted at 200°. When mixed with pure tephrosin (melting point 198°), the melting point was depressed (165–175°).

Anal. Calcd. for $C_{25}H_{24}O_8$: C, 66.35; H, 5.35; OCH_3 (2), 13.72. Found: C, 66.36; H, 5.42; OCH_3, 14.2.

Tephrosin Monocarboxylic Acid.—A mixture of 0.5 g. of tephrosin dicarboxylic acid and 5 cc. of diphenyl ether was heated to its boiling point for approximately one-half minute. During the process the liquid rapidly acquired a bright yellow color as a result of dehydro formation. The solution was then cooled and quickly diluted with three volumes of methanol, causing crystallization to take place immediately. The product

(250 mg.) consisted of bright yellow rods whose melting point was 269° with decomposition.

For analysis, 250 mg. of the acid was dissolved in the necessary quantity of alkali, the solution was diluted with water to 2 liters and then acidified with acetic acid. The material separated as pale yellow hair-like crystals which began to sinter and darken at 250° and melted with decomposition at 268–269°. A saturated alcoholic solution of the material gave a pink color with ferric chloride.

Anal. Calcd. for $C_{19}H_{14}O_8$: mol. wt., 370.2; C, 61.61; H, 3.81; OCH_3 (2), 16.76. Found: mol. wt., acid titration, 370; C, 61.71; H, 3.95; OCH_3, 16.8.

α-Hydroxyisobutyric Acid from Tephrosin Dicarboxylic Acid.—The methanol–diphenyl ether mother liquor from the experiment above was diluted with water, made strongly alkaline and extracted with ether. The aqueous solution was then acidified and again extracted with ether. This extract was dried, the ether was removed and the residue, contained in a test-tube, was gently heated under reduced pressure. A very small quantity of α-hydroxyisobutyric acid sublimed upon the cool portion of the tube. There was, however, a sufficient quantity to identify it by its melting point and its characteristic property of subliming at approximately 50°.

Acetyl Tephrosin Monocarboxylic Acid.—A solution of 0.2 g. of tephrosin monocarboxylic acid in a mixture of 2 cc. of acetic anhydride and 2 cc. of pyridine was allowed to stand at room temperature for two days. During the process 0.2 g. of the acetyl derivative separated. It was dissolved in the necessary quantity of boiling butanol, and this solution was diluted with 5 volumes of ethanol. In a short time the material separated as aggregates of small extremely thin yellow rods, which when rapidly heated began to melt at approximately 230° and decomposed at 250–255°. It gave no color reaction with ferric chloride.

Anal. Calcd. for $C_{21}H_{16}O_9$: C, 61.16; H, 3.91; OCH_3 (2), 15.06. Found: C, 60.75; H, 4.07; OCH_3, 15.7.

Risic Acid from Tephrosin Monocarboxylic Acid.—A solution of 0.5 g. of tephrosin monocarboxylic acid in 10 cc. of 10% potassium hydroxide solution was treated with 3 cc. of 30% hydrogen peroxide, according to the directions for the preparation of derric acid.[1b] When the reaction was completed the solution was diluted to 50 cc. and acidified with sulfuric acid. Two hundred and fifty mg. of risic acid (melting point, 256°) separated and was identified by comparison with an authentic sample of the acid.

Tephrosic Acid from Tephrosin Monocarboxylic Acid.—Tephrosic acid was prepared by hydrolyzing tephrosin monocarboxylic acid with 10% alcoholic potassium hydroxide, according to the directions recorded for the preparation of deguelic acid.[1a] Acidification of the resultant solution caused the separation of tephrosic acid as beautiful colorless crystals which melted at 196°. Their solution gave a brownish pink color with ferric chloride but because of lack of material[11] the study of this compound has not been concluded. A complete description of its properties, therefore, cannot be presented at this time. For the purpose at hand, however, the fact that the compound is formed is sufficient evidence to indicate that tephrosin monocarboxylic acid is a dehydro derivative.

Summary

Evidence has been presented to indicate that deguelin may be represented by formula I in the text.

[11] Our last shipment of cubé roots, upon which we depend for tephrosin and its derivatives, was unusual in that its rotenone content was very high (11%) and the deguelin obtained from the rotenone mother liquors was almost chemically pure. The extract, however, contained no tephrosin. It is therefore necessary to await a satisfactory supply of cubé root from South America before completing the study of tephrosic acid.

It has also been shown that tephrosin is a hydroxydeguelin and that the hydroxyl group in tephrosin occupies the position of one of the hydrogen atoms attached to either carbon atom 7 or 8 in the deguelin formula.

WASHINGTON, D. C.

NOTES

The Decomposition of *n*-Valerolactone

BY RALPH W. THOMAS AND H. A. SCHUETTE

Proof has already been presented[1] in support of the statement that *n*-valerolactone will not withstand distillation at atmospheric pressure—reports to the contrary notwithstanding—since it undergoes partial decomposition as it approaches its boiling point. The nature of this decomposition has now been traced to the formation, in the main, of a polymerization product, and an explanation has been found for the discrepancies in the vapor pressure curves of this compound when obtained by two different methods of procedure, a dynamic[2] and a static.[3] How the former conclusion has been arrived at is summarized in this communication.

In order to fix a point of departure in the study of this problem, the assumption was made that the decomposition in question is accompanied by the evolution of carbon dioxide and the formation of a butene (2:3 or 1:2). The set-up in which the decomposition studies were carried out closely simulated the conditions which obtain in the determination of pressure–temperature relationships. To that end the lactone was heated under thermostatically controlled conditions in a 2.5-cc. bulbous glass decomposition chamber to which had been sealed an 8-mm. delivery tube provided with a short upright side arm which was later to serve the dual purpose of introducing or removing samples and as an aid in sweeping out the air from the apparatus with nitrogen. At a distance of about 25 mm. from this side arm, the tube was bent at an angle of 45°; beyond that, as a precautionary measure against loss of material during heating, it took the form of a spiral condenser. A delivery tube leading from the latter to an inverted, mercury-filled buret completed the system.

That the reaction herein involved is not wholly due to a decarboxylation with the formation of a butene was shown by the fact that a 3.16-g. sample yielded only about 1 cc. of gas on heating for 530 hours at 202 ± 0.5°, which is four degrees below the alleged boiling point of this compound at atmospheric pressure. Although this gas was found to contain some carbon dioxide, yet no evidence could be secured that ethylenic hydrocarbons had been formed in the decomposition. A repetition of the

[1] Schuette and Thomas, THIS JOURNAL, **52**, 2028 (1930).

[2] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

[3] Smith and Menzies, THIS JOURNAL, **32**, 1412 (1910).

experiment during the course of which, at three time intervals, samples were removed for ultimate analysis showed that the residue, except for change in color, had altered only slightly during a 773-hour heating, having changed from C = 59.58 and H = 8.17 to C = 59.32 and H = 7.74. For these reasons it appears quite probable that the main course of the reaction is such as to favor the formation of a polymerization product. Further support for this conclusion may be found in the fact that the observed vapor pressures[1] when measured by a dynamic method[2] were lower than the calculated at any given temperature above that at which this compound begins to decompose. This is to be expected were a polymerization takes place.

The static method[3] of measuring pressure–temperature relationships which was employed is very susceptible to the influence of gaseous decomposition products even though their quantity may be small. An immediate effect of this characteristic is to be found in the higher values which were obtained by this method of measurement. The foregoing observations account, it seems, for the discrepancies which were previously noted in vapor pressure measurements by two different methods of approach.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

RECEIVED FEBRUARY 23, 1932
PUBLISHED JULY 6, 1932

Preparation and Properties of the Normal Barium Salt of *l*-Cystine.[1]

BY CLIFFORD J. B. THOR AND ROSS AIKEN GORTNER

Several normal metallic salts of cystine have already been described. In 1900, Embden[2] prepared the normal copper salt and employed it in the isolation of the amino acid. A little later, Neuberg and Mayer[3] prepared the corresponding salts of silver, mercury, lead and cadmium as well as of copper. Recently, Toennies and Lavine[4] have succeeded in obtaining the lithium, sodium and potassium salts of cystine in crystalline form.

In the course of a study of the alkaline decomposition of cystine, which will be presented in a separate paper, it was observed while adding crystalline barium hydrate to a hot aqueous suspension of *l*-cystine that most of the cystine went into solution at a certain stage and that immediately thereafter a pale yellow precipitate separated out. By filtering off this pre-

[1] Published as Paper No. 1079, Journal Series, Minnesota Agricultural Experiment Station. Abstracted from a thesis submitted by Clifford J. B. Thor to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1931.

[2] Embden, *Z. physiol. Chem.*, **32**, 94 (1901).

[3] Neuberg and Mayer, *ibid.*, **44**, 498 (1905).

[4] Toennies and Lavine, *J. Biol. Chem.*, **90**, 203 (1931).

cipitate at once, washing it with a small amount of water, then with alcohol and ether and finally drying at 105°, a product was obtained (Preparation I) which analyzed fairly well for the normal barium salt of cystine.

Since no mention of this substance could be found in the literature and since it is involved in studies dealing with the decomposition of cystine by alkalies, it was thought desirable to prepare the salt in pure form and to determine its more important properties.

Method of Preparation.—A very satisfactory method consists in mixing equivalent amounts of aqueous $Ba(OH)_2$ and cystine in the cold and precipitating the resulting salt with alcohol. More exactly, 16 g. of $Ba(OH)_2 \cdot 8H_2O$ was dissolved in 250 cc. of boiled distilled water and cooled to 0°. Then 12 g. of the *l*-cystine was added and the mixture shaken in a stoppered Erlenmeyer flask until only very little undissolved material remained. The cold mixture was filtered through a Buchner funnel and after washing with distilled water the slight residue was discarded. The combined filtrate and washings, amounting to about 300 cc., were treated with 1600 cc. of 95% ethyl alcohol, which caused abundant precipitation of a white granular material. After thorough shaking, this mixture was placed in a refrigerator at −15° overnight. In the morning, the precipitate was filtered off with suction, washed with 600 cc. of 95% ethyl alcohol, then with ether and finally dried in an air oven at 100°. The yield was 18.1 g., which is 96.5% of the theoretical calculated from the cystine taken.

Properties.—The above product (Preparation II) was a perfectly white, finely divided powder which under the microscope showed no clearly defined crystalline form.

Anal. Calcd. for $C_6H_{10}O_4N_2S_2Ba$: N, 7.46; S, 17.07; Ba, 36.57. Found: N (Prepn. I), 7.32, (Prepn. II), 7.31; S (I), 16.20, (II) 16.65; Ba (I), 35.78; (II) 36.42.

A saturated solution of the salt was prepared by shaking 4 g. with 50 cc. of distilled water, allowing it to stand overnight at 25°, and filtering to remove excess salt. The saturated solution was very faintly yellow in color but seemed to be perfectly stable under the conditions of observation. Forty cc. of this solution was diluted to 200 cc. with water and aliquots were taken for nitrogen, sulfur and barium analyses to determine solubility, as indicated. This new salt of cystine then is water soluble at 25° to the extent of 6.15 g. per 100 cc. of saturated solution.

SOLUBILITY OF THE NORMAL BARIUM SALT OF *l*-CYSTINE IN WATER AT 25°

Basis of calculation.....	Nitrogen content	Sulfur content	Barium content	
Barium salt in 100 cc. of satd. soln.....	6.14	6.17	6.14	Av. 6.15

When placed in a 1-decimeter tube, the saturated solution gave a saccharimeter reading of −11.0° at 25° and on dilution to five times its volume with water a proportionate value of −2.2°. Calculated on the basis of concentration of the barium salt, this gives a specific rotation of −61.9°; or calculated for cystine contained in the salt, of −96.9°. The latter agrees quite well with similar figures reported by Toennies and Lavine[4] for the lithium, sodium and potassium salts of cystine. Free cystine was isolated from some of the salt and 0.2 g. of this dissolved in 25 cc. of normal hydrochloric acid at 25°, when placed in a 1-decimeter tube, gave a reading of −4.6° saccharimeter units. The corresponding specific rotation of −199.1° as compared with −204.2° for the original cystine indicates that racemization had not occurred to any considerable extent during the formation of the barium salt. Hence, it is safe to conclude that Preparation II consisted almost entirely of the barium salt of *l*-cystine.

If the saturated aqueous solution of the substance is diluted sufficiently with water,

hydrolysis takes place and a portion of the cystine precipitates out in the form of hexagonal plates. That hydrolysis had not taken place in preparing the saturated solution is clearly shown by the very close agreement between solubilities calculated from contents of nitrogen and sulfur on the one hand and barium on the other.

When the dry salt was heated in a melting point tube it showed no signs of decomposition or fusion up to about 250°; then it began to brown very gradually but without sintering.

When a portion of the salt equivalent to 2.5 g. of cystine was refluxed with 50 cc. of distilled water for twelve hours, nitrogen and sulfur analyses made after the removal of free hydrogen sulfide and ammonia indicated that decomposition to the extent of approximately 50% had taken place.

In its property of being water soluble, the barium salt of *l*-cystine resembles the alkali salts and differs from the heavy metal salts so far described. This characteristic as well as its ease of preparation and the ease of determination of its metallic constituent should make the barium salt useful in further studies on the mechanism of the alkaline decomposition of cystine. It might also find use in the preparation of derivatives of cystine, particularly in cases where the reaction requires anhydrous conditions.

CONTRIBUTION FROM THE
DIVISION OF AGRICULTURAL BIOCHEMISTRY
UNIVERSITY OF MINNESOTA
ST. PAUL, MINNESOTA

RECEIVED MARCH 17, 1932
PUBLISHED JULY 6, 1932

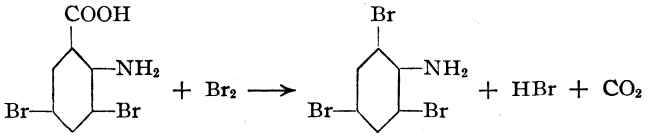
The Structure of the Bromination Product of Ortho-Nitrotoluene

BY DAVID L. YABROFF

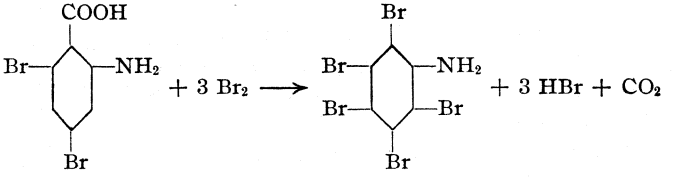
Wachendorff[1] obtained a dibromo product upon the bromination of *o*-nitrotoluene which he called a dibromonitrotoluene. He made the observation, however, that this product was soluble in alkali. Greiff[2] showed that the compound was a dibromo-anthranilic acid and suggested that it might be the *p-m*-dibromo-anthranilic acid obtained by Hübner[3] upon the nitration and reduction of *p-m*-dibromobenzoic acid since both of the products melted at 225°.

If an intramolecular oxidation and reduction of the nitrotoluene occurs before the bromination, we should expect 3,5-dibromo-2-aminobenzoic acid as the final product. If bromination occurs before the oxidation–reduction process, we should expect 4,6-dibromo-2-aminobenzoic acid to be formed. These two compounds may be readily distinguished by allowing them to react for twenty-four hours in a dilute alcoholic solution with bromine water in the presence of a mineral acid. Under these conditions[4,5] all positions ortho or para to the amino group which are not already substituted are brominated, and at the same time bromine is substituted for the carboxyl group. This may be represented as

[1] Wachendorff, *Ann.*, **185**, 259 (1877).
[2] Greiff, *Ber.*, **13**, 288 (1880).
[3] Hübner, *ibid.*, **10**, 1706 (1877).
[4] Francis and Hill, THIS JOURNAL, **46**, 2498 (1924).
[5] Flürscheim and Holmes, *J. Chem. Soc.*, 448 (1928).



Oxidation–reduction occurring first



Bromination occurring first

In one case we would obtain tribromoaniline, in the other case pentabromoaniline. The product actually obtained by this treatment was tribromoaniline—m. p. 119°, mixed m. p. 120°; bromine analysis (Carius),[6] found 72.3, 72.2%; calcd. for $C_6H_2NH_2Br_3$: 72.7.

These results indicate that the oxidation–reduction process of the nitrotoluene occurs first and the anthranilic acid formed is then brominated, giving rise to the 3,5-dibromo-2-aminobenzoic acid. Wheeler and Oates[7] obtained this compound (m. p. 232°) by the direct bromination of anthranilic acid.

[6] These analyses were carried out by Mr. Leslie H. Bayley.

[7] Wheeler and Oates, THIS JOURNAL, **32**, 770 (1910).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

RECEIVED MARCH 25, 1932
PUBLISHED JULY 6, 1932

The Isomeric Desoxybenzanisoins

BY JOHANNES S. BUCK AND WALTER S. IDE

In a recent paper[1] S. S. Jenkins criticizes some of our work,[2] being apparently unable to reproduce certain of our results. The Friedel and Crafts reaction which is in question goes unusually well, and we have repeated the other two questioned preparations, with results identical to those which we reported previously.

We desire to correct Jenkins' statement that, with regard to the reduction of benzanisoin to *p*-methoxybenzyl phenyl ketone, we reported none of the isomeric ketone. On the contrary we specifically stated[3] that isomeric ketones might be present but that no serious attempt to isolate these was made. Jenkins neglects to mention that we proved the structure of our compounds by the Beckmann reaction. His work

[1] Jenkins, THIS JOURNAL, **54**, 1155 (1932).

[2] Buck and Ide, *ibid.*, **53**, 1536 (1931).

[3] Ref. 2, p. 1538.

has not contradicted any of our conclusions as to the structures of the compounds obtained by us.

In view of the difficulties which have arisen, we submit descriptions of the methods of preparation in question at greater length. The preparations have been checked, and we reaffirm our earlier statements.

Benzyl *p*-Methoxyphenyl Ketone.—15.5 g. of phenylacetyl chloride[4] and 13.0 g. of anisole (calcd. 10.8) were dissolved in 100 cc. of carbon bisulfide (Baker C. P.), in a flask fitted with a reflux condenser and a wide tube for adding the aluminum chloride; 15.0 g. of powdered aluminum chloride (Baker, anhydrous, C. P.) was then added in portions over thirty minutes. The bisulfide refluxes gently during the addition, and hydrogen chloride is evolved. The mixture becomes deep crimson in color and a dark crimson oil sinks to the bottom. After standing at room temperature for a further ninety minutes, 150 g. of crushed ice was added and then 20 cc. of concd. hydrochloric acid. The bisulfide layer was separated and washed twice with dilute hydrochloric acid (further bisulfide being added if the product starts to separate). The bisulfide was then evaporated on the steam-bath, 100 cc. of water added and steam bubbled through for ten minutes. On cooling the product solidified, and was then filtered off, washed with water, drained and dissolved in hot alcohol. On standing the ketone crystallized out. The melting point was 72°, raised to 74–75° on recrystallization. On three consecutive runs the yields were 19.4, 18.3 and 19.0 g., average, 84%. A further quantity (about 1.5 g.) may be obtained on diluting the liquors. Washing with alkali is unnecessary.

***p*-Methoxybenzyl Phenyl Ketone.**—50.0 g. of benzanisoin was dissolved in 200 cc. of 96% alcohol, in a flask fitted with a reflux condenser; 50.0 g. of mossy tin and 50.0 cc. of concd. hydrochloric acid were added, together with 0.5 g. of copper sulfate. The mixture was refluxed on the steam-bath for twelve to fifteen hours, a little (0.5 g.) copper sulfate being added occasionally as the reaction slowed down. After the first six hours, an additional 50 cc. of concd. hydrochloric acid was added to the mixture. When the reaction was complete, the mixture was filtered hot, the product rapidly crystallizing out on cooling. After standing, it was filtered off and washed with water, and then with cold alcohol; yield (unrecrystallized) 87%. Recrystallized from alcohol, the product melted at 91–92° and weighed 37.7 g. (82%). The melting point is raised to 94° after two further recrystallizations. The writers were unable to obtain a pure specimen of benzyl *p*-methoxyphenyl ketone from the liquors of this preparation.

Oximes of *p*-Methoxybenzyl Phenyl Ketone.—14.4 g. of *p*-methoxybenzyl phenyl ketone was dissolved in 100 cc. alcohol (96%) and hydroxylamine acetate solution (from 8.0 g. hydroxylamine hydrochloride and 13.0 g. potassium acetate) added. The reaction mixture was kept at 40–50° for two hours, when crystals commenced to separate. The mixture was then put in a cold place (0°) overnight and the crystals which formed were filtered off next day. After one recrystallization from alcohol the melting point was 132°. The liquors, after evaporation under reduced pressure, deposited a product, which, recrystallized several times from alcohol, melted at 95–96° (previously reported as 94°). The yield of the *anti* oxime (m. p. 132°) is about 10 g. and that of the *syn* oxime about 2 g., the relative amounts varying somewhat in different preparations.

Erratum.—In the paper in question,[2] p. 1540, line 19, for "Ketone E" read "Benzoin 5."

THE EXPERIMENTAL RESEARCH LABORATORIES
BURROUGHS WELLCOME AND CO.
TUCKAHOE, N. Y.

RECEIVED APRIL 25, 1932
PUBLISHED JULY 6, 1932

[4] Vanino and Thiele, *Ber.*, **29**, 1727 (1896).

COMMUNICATIONS TO THE EDITOR

3-FURALDEHYDE (3-FURFURAL)

Sir:

"Furfural" or 2-furaldehyde was first obtained one hundred years ago [Döbereiner, *Ann.*, **3**, 141 (1832)]. Its isomer, 3-furaldehyde or 3-furfural, has now been synthesized by the following sequence of reactions: malic acid ⟶ coumalic acid ⟶ methyl coumalate ⟶ methyl bromocoumalate ⟶ 2,4-furandicarboxylic acid ⟶ 3-furancarboxylic acid ⟶ 3-furoyl chloride ⟶ 3-furaldehyde.

The odor of 3-furaldehyde is more remindful of benzaldehyde than is 2-furaldehyde. Some physical constants are: b. p. 144° (732 mm.); n_D^{20} 1.4945; sp. gr. $\frac{20}{20}$ 1.111. The phenylhydrazone melts at 149.5°.

3-Furanaldehyde responds to the usual aldehyde tests but *unlike* 2-furanaldehyde it gives no color test with aniline acetate. We have also noted that 2,4-dimethyl-3-furfural gives no aniline acetate test. The new aldehyde appears to be more highly resistant to auto-oxidation than might have been predicted, and is more stable than its isomer.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
ROBERT R. BURTNER

RECEIVED MAY 31, 1932
PUBLISHED JULY 6, 1932

THE VELOCITY OF DISSOCIATION OF NITROGEN TETROXIDE BY THE METHOD OF SOUND WAVES

Sir:

In a communication from this Laboratory [Kistiakowsky and Richards, THIS JOURNAL, **52**, 4661 (1930)] it has been demonstrated that with an experimental accuracy of 0.5%, no change in the velocity of sound in nitrogen tetroxide is detected at 25° with frequencies between 9 and 80 k.c. The lower limit thus set for the velocity of dissociation ($k = 5 \times 10^4$) according to the reasoning of Einstein [*Sitz. Akad.*, 380 (1920)] closely approximates the value (k = about 1×10^5) which is obtained from the kinetic theory of gases as the maximum reasonable upper limit. Brass and Tolman [THIS JOURNAL, **54**, 1003 (1932)] by another method have recently obtained positive evidence of the rate of dissociation, and assign to the velocity constant at 25° an order of magnitude (k = 2.2 to 8.4 $\times 10^4$) which accords with these conclusions.

It is now possible to obtain more specific information concerning this reaction by the acoustical method. Apparatus of special design has permitted the study of the velocity of sound in nitrogen tetroxide between 1.0 and 30° and from 130 to 760 mm. pressure at frequencies between 9 and 93 k.c. At 260 mm. pressure and 30° a further study has been made

between 90 and 500 k.c. In both cases the reproducibility of the measurements has proved to be 0.05%. A wall-correction has been evaluated and applied.

The correspondence between measured velocities at zero frequency and those calculated from Einstein's equations is excellent at 260 mm., and indicates that the assumptions underlying the theoretical reasoning may be applied with confidence to the interpretation of these measurements. Since the absorption coefficient is not found to increase noticeably even at 500 k.c., similar reasoning appears legitimate over the entire frequency range which has been studied. Granting this, a straightforward picture of the kinetics of dissociation emerges. The velocity constant at 25° and 260 mm. is approximately 4.8×10^4, and the activation energy of dissociation approximates closely to the heat of dissociation of nitrogen tetroxide. It may be assumed, therefore, that the velocity of association of nitrogen dioxide has little if any temperature coefficient. The velocity of dissociation decreases with decreasing pressure. These conclusions are independent of unavoidable uncertainties concerning the heat capacities of the dioxide and tetroxide molecules, the exact value of the heat of dissociation, and the exact absolute values of the velocity of sound in nitrogen tetroxide at zero frequency.

Recent evidence that the vibrational specific heat terms in carbon dioxide may become inactive at high frequencies of sound [Kneser, *Ann. Physik*, [V] **11**, 777 (1931)] has suggested the possibility that a similar effect may appear in nitrogen tetroxide, and has caused a delay of some months in the publication of the conclusions outlined above. It is hoped that the temperature coefficient of the divergence between high and low frequency velocities of sound will provide a means to differentiate between this effect and that discussed by Einstein. When an experimental distinction between the two has been established, the measurements on nitrogen tetroxide will be submitted in detail for publication.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

WILLIAM T. RICHARDS
JAMES A. REID

RECEIVED JUNE 2, 1932
PUBLISHED JULY 6, 1932

THE INVERSION OF CRISTOBALITE

Sir:

Supplementing the foregoing note by Dr. J. W. Greig (p. 2846), I may be permitted to quote from a letter received recently from Dr. K. Endell, one of the observers referred to in my discussion of the inversion of cristobalite. Dr. Endell says (in translation): "It appears to me very improbable that this inversion can be delayed. My early observations are probably not entirely conclusive. In recent years I have tested hundreds

of silica brick, and also ceramic bodies which contain cristobalite, for their thermal dilatation upon heating and cooling. The result has invariably been that upon cooling the volume contraction associated with the alpha–beta cristobalite inversion takes place without a time lag. The cases observed by Greig in glass and by Levin and Ott in opals are not known to me. As you correctly state, however, this is different from the delay of the inversion by quenching."

Dr. Olaf Andersen and I have tried several ways of quenching free cristobalite from a temperature above its high-low inversion point, but it has always inverted without delay. The inhibition of the inversion in crystals embedded in a glassy matrix, as observed by Greig and by Levin and Ott, deserves further study for the light it may throw on the atomic mechanism of such inversions.

RESEARCH LABORATORY
UNITED STATES STEEL CORPORATION
KEARNY, NEW JERSEY
ROBERT B. SOSMAN

RECEIVED JUNE 3, 1932
PUBLISHED JULY 6, 1932

NEW BOOKS

Von Davy und Döbereiner bis Deacon, ein halbes Jahrhundert Grenzflächenkatalyse. (From Davy and Döbereiner to Deacon; A Half Century of Contact Catalysis.) By ALWIN MITTASCH, Director of the Oppau Research Laboratories of the I. G. Farbenindustrie A.-G., and ERICH THEIS. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. 278 pp. 14 Figures and 16 Portrait Inserts. 17 × 23.5 cm. Price, Mk. 18.50.

In the study of a phenomenon such as catalysis, which is still the object of intensive investigation and which makes its appearance in every branch of chemistry, it is important to attain an historical perspective. This will be greatly facilitated by the present volume which is an historical study of the earlier stages in the development of our knowledge of heterogeneous catalysis. It presents meticulously and sympathetically the work of scores of investigators; for instance, the discoveries of Davy, Thénard, Döbereiner and Schönbein, and the theoretical contributions of Berzelius, Liebig and the less widely known Bellani, Mercer and Playfair.

In addition, there are special chapters on the beginnings of the sulfuric acid contact process, and of the processes for the catalytic synthesis and oxidation of ammonia.

The authors have also succeeded, by means of many footnotes and excellent portraits, in maintaining that connection between personalities and ideas which is so advantageous in an historical treatise.

ARTHUR B. LAMB

Lehrbuch der Radioaktivität. (Textbook on Radioactivity.) By GEORG V. HEVESY and FRITZ PANETH. Second, fully revised edition. Verlag von Johann Ambrosius Barth, Salomonstrasse 18 B, Leipzig C 1, Germany, 1931. xii + 287 pp. 50 figs. 16 × 23.5 cm. Price, RM. 19.80; bound, RM. 21.60.

The first German edition of this excellent little text appeared in 1923. Three years later, the Oxford Press brought out an English translation by R. W. Lawson of an enlargement of the first edition, which amounted almost to a second edition in itself. As a textbook of radioactivity for college use, this work has proved so acceptable that the present second edition is sure to find a ready welcome.

A complete revision has been effected with the addition of much new material. The newest phases of radioactivity and nuclear chemistry and physics are discussed, such as the relation between alpha, beta and gamma radiation and the structure of the nucleus, the nature of cosmic rays, and the ultra-gamma radiation produced by bombarding certain lighter nuclei with alpha particles. The application of wave mechanics to the escape of particles from the nucleus through an energy barrier is well presented. The chapters on isotopy, on radioactive substances as indicators, on packing effect and the deviation of atomic masses from whole numbers are especially well done, as well as the chapter on the importance of radioactivity in geology and in cosmic chemistry and physics.

The reviewer's impression is strengthened by the second edition that this work is much too scholarly and broad in its scope to be regarded merely as an elementary text. The need for literature references especially in the newest fields will be keenly felt by many readers. Such addition in a succeeding volume appears to be all that is lacking to raise this otherwise splendid work to the dignity of an elementary treatise.

S. C. LIND

Katalyse vom Standpunkt der chemischen Kinetik. (Catalysis from the Point of View of Chemical Kinetics.) By GEORG-MARIA SCHWAB, Lecturer in Chemistry at the University of Munich. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1931. viii + 249 pp. 39 figs. 16 × 24 cm. Price, RM. 18.60; bound, RM. 19.80.

The last decade witnessed a rapid progress of the kinetic theory of catalysis and the appearance of a book by G.-M. Schwab dealing with this subject is very timely.

In a rather limited space the author succeeds in giving a good review of the stand of knowledge (at the end of 1930) concerning the following subjects: homogeneous catalysis of simple and chain reactions in gases; homogeneous catalysis by intermediary products and by ions in solutions; solvent action; heterogeneous gaseous reactions and the theory of ad-

sorption of gases; colloid catalysis and enzyme action. The author has succeeded very well in creating as clear a presentation as could be expected in a rapidly developing branch of science. At the same time, the book is sufficiently complete to acquaint the reader with all significant developments of the theory and with the more essential experimental contributions.

Some rather insignificant mistakes have been noticed. Thus on p. 21 the author counts translation among degrees of freedom active in unimolecular decompositions; on pp. 201–202 the length of edges of a crystal is considered to be proportional to the square of the surface area of the crystal. On p. 168 the proof of the (quite correct) assertion that the catalytic action of a solid surface is due not entirely and not principally to a condensation of the reactants is not convincing. The reviewer cannot agree with the statement (pp. 141–142) that the "semi-thermodynamic" derivation of the Langmuir adsorption isotherm by Volmer is to be preferred to the original treatment, since the Volmer argument assumes complete freedom of motion of the adsorbate on the surface, something which may be seriously doubted in many cases important in catalysis and an assumption unessential to the purely kinetic elementary treatment of the problem.

In conclusion the reviewer would like to recommend this book to all those who are interested in catalysis and who have already some knowledge of the general kinetic theory of reaction velocities.

G. B. KISTIAKOWSKY

Electrical Phenomena in Gases. By KARL KELCHNER DARROW, Ph.D., Research Physicist, Bell Telephone Laboratories. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Maryland, 1932. xvii + 492 pp. 91 figs. 15.5 × 23.5 cm. Price, $8.00.

This is the second book by the author on recent developments in modern physics; the first, "An Introduction to Contemporary Physics," was published in 1926 by Van Nostrand.

The second book is the only one on this subject published in this country and brings up to date the information concerning the electrical phenomena in gases. The book is written by a physicist from a physicist's point of view. The style, which is excellent and original, is characteristic of the man and so quite human. The subject matter is well chosen from a mass of material published over years. The bibliography is very extensive and well chosen but necessarily not complete. Complicated and not well understood experiments and phenomena are presented in a clear and well-digested form. The context is largely descriptive of carefully selected typical experiments with an evaluation of the results together with numerous suggestions as to the next step or experiment to be done in the

respective fields. Mathematical equations and theoretical developments are reduced to a minimum.

The author and subject index on this broad and much worked subject is very useful and is to be commended. However, it is much to be regretted that the table of contents consists only of listing the titles of the chapters. While these titles may be well chosen, they cannot and do not represent the wealth of subjects or subject matter discussed in the respective chapters. An explanation of the origin and functions of the various elements and factors concerned in a conducting gas in an electric discharge such as electrons, ions, normal and excited atoms and molecules, photons, radiation, visible and invisible, electric potential, field strength, excitation, ionization and collision phenomena play the major roles in this treatise.

The first four chapters deal with elementary processes in a very rarefied atmosphere and may be attributed to single electrons, single ions or single atoms. The next five chapters dy contrast deal with phenomena at higher pressures up to atmospheric where an ion is forced to make many collisions with a resulting current drift superimposed upon the random velocities of the electrons, atoms and excited molecules. These chapters are largely concerned with the phenomena of mobility, diffusion, recombination and attachment, self-amplified ionization and breakdown in the gaseous system. The last three chapters are concerned with the glow and arc discharges. Elaborate and painstaking efforts to bring about order and understanding out of chaotic complex phenomena are much in evidence, unfortunately, however, without entire success, leaving much to be desired until the arc is better understood. The exploring electrode method of investigation is described. The results are interpreted in the form of "space charge," "sheaths" and "plasma," these terms being the added technology employed within the last decade.

The publishers are to be commended on the general appearance and the clarity of type and figures of this volume which should add considerably to the pleasure of the reader.

C. H. KUNSMAN

Chemische Bindung als elektrostatische Erscheinung. (Chemical Combination as an Electrostatic Phenomenon.) By A. E. VAN ARKEL AND J. H. DE BOER. Authorized German translation by Li Klemm and Wilhelm Klemm. With a Word of Accompaniment by Wilhelm Biltz. Verlag von S. Hirzel, Königstrasse 2, Leipzig C 1, Germany, 1931. xx + 320 pp. 71 figs. 15 × 23 cm. Price, RM. 15; bound, RM. 17.

It is not without reason that this book has three prefaces and an eight-page "glossary of the most important concepts," for, as expressed in the "Geleitwort:" "I believe I am making no subjective statement when I

assert that never before in the history of chemistry has the chemist encountered questions of equal theoretical difficulty. Not difficulties of the formal mathematical sort, the mathematician will gladly undertake to overcome those for us, but *conceptual* difficulties." And it is typical of the state of the subject that after ten chapters of fairly successful explanation of chemical combination in purely electrostatic terms, the authors should begin the last chapter with the confession: "So long as we have to do with combination between *unlike* atoms, we reach in very many cases a satisfactory representation by assuming that the atoms bear opposite electric charges, *i. e.*, have thus become ions. As has previously been shown, we can derive from this an essential part of the properties of compounds.

"This conception of valence force is however not suitable for *all* cases; in particular it leaves us completely in the lurch when it is a question of combinations between *like* atoms."

The key to the paradox is perhaps to be found in the proof on p. 55 that changing the exponent of distance in the expression for the Born repulsion force from 10 to 9 makes only a little over one per cent. difference in the lattice energy. As, in the calculus, second differentials need be considered only when first differentials vanish; so, in valence theory, Coulomb's law forces, when present, may swamp the other terms in the expression for the energy of combination. Since, however, the energies of formation of symmetrical diatomic molecules are of the same order as those of unsymmetrical molecules, there must be many cases in which only the present roughness of our measurements makes a neglect of homopolar energy terms tolerable.

The book is a translation of a compilation of articles which appeared in 1929 in the *Chemisch Weekblad*. At a time when the chemical pendulum has swung so far away from Berzelius, such a volume is of value in attaining a proper mental balance.

ELLIOT Q. ADAMS

Kolloidchemische Technologie. Ein Handbuch kolloidchemischer Betrachtungsweise in der chemischen Industrie und Technik. (Colloid-Chemical Technology.) Edited by Dr. RAPH. ED. LIESEGANG, Frankfurt A.M. Second, completely revised edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1932. viii + 1085 pp. 376 figs. 18.5 × 26.5 cm. Price, RM. 68; bound, RM. 72.

The present edition of this book does not differ materially in content or organization from the first edition, which preceded it by only four years. In general, the various topics are treated by the same co-authors who contributed to the first edition, but new chapters relating to lipoids, sugar, insecticides and fertilizer have been added. The "theoretical part,"

which filled about a quarter of the first edition, is now limited to two short chapters, and on this account the new edition is not much larger than the previous one. Most of the chapters have been brought up to date by the addition of such new material as is warranted by recent progress, though it is probably not to be expected that industrial practice has changed very much in such a short time. In the chapter on the textile industry, no mention is found of the excellent work published from the British laboratories devoted to wool and cotton, and only a single reference to work done since 1926. By contrast, the chapter on "artificial silk" has been brought up to date in the most thorough manner, and this may be said also of nearly all the chapters. The attractive typographical style of the previous edition has been retained, and the material has been thoroughly indexed.

E. B. MILLARD

Organic Syntheses. Collective Volume I, being a Revised Edition of Annual Volumes I–IX. HENRY GILMAN, Editor-in-Chief, ROGER ADAMS, W. H. CAROTHERS, H. T. CLARKE, J. B. CONANT, C. S. MARVEL, C. R. NOLLER, F. C. WHITMORE, C. F. H. ALLEN, Secretary. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. ix + 564 pp. 15.5 × 23.5 cm. Price, $6.00.

In the preface to the "Collective Volume" the reasons for collecting the material contained in the first nine volumes of "Organic Syntheses" are stated in the following terms: "There are several objectives for this Collective Volume, the realization of which, it is hoped, will extend the usefulness of the series. First, it is convenient to have a large number of preparations in a single volume. Second, new and improved directions are included to replace or supplement earlier preparations. The new directions are for adipic acid, benzilic acid, cyclohexylcarbinol, dibenzoylmethane, *d*-glutamic acid, glycine *dl*-methylethylacetic acid, pentaerythritol and *n*-propylbenzene. Third, a large number of relatively minor but significant corrections have been made, and many suggestions have been incorporated for improving specific preparations. Fourth, the large number of preparations contained in a collective volume makes it more practicable to have several useful indexes."

The editors manifestly have spared no effort to make the volume as useful as possible. Besides arranging all preparations in alphabetical order, they have supplied the volume with five indexes, including one in which preparations are listed with respect to the type of reaction that is employed, and another in which they are classified with respect to the type of compound that is formed.

The publishers have done their part in making an attractive volume, and the edition is so free from typographical errors that the reviewer takes some pride in having discovered "glucol" on page 286.

E. P. KOHLER

Esercizi Numerici di Chimica Organica. (Numerical Exercises in Organic Chemistry.) By Professor GUIDO BARGELLINI, University of Rome. Editrice Studium, Piazza S. Agostino 20-a, Rome, Italy, 1931. 242 pp. 13.5 × 19.5 cm. Price, 25 lire.

This book consists of three parts. The first of these sets forth the methods of determining molecular formulas from analytical data. The second part presents fifty problems, detailed solutions of which make up the third part. Each problem describes a compound by giving analytical data from which one may calculate the empirical formula and the molecular weight. Characteristic reactions and properties follow and from these it is possible to identify the compound.

The problems deal with a wide variety of important types of organic compounds and require the student to possess and to use a large amount of information on the subject. There is enough of the puzzle element involved to make the exercises fascinating, and there can be no doubt that the author has hit upon an excellent scheme for impelling students to think.

Although this book is novel in type, problems of a similar sort have been rather widely used in this country in connection with courses in qualitative organic analysis. However, no collection of such problems has as yet been published in English and for this reason this book should be welcomed by all teachers of organic chemistry.

REYNOLD C. FUSON

Principles of Soil Microbiology. By SELMAN A. WAKSMAN. Second edition, thoroughly revised. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Md., 1932. xxviii + 894 pp. 15.5 × 23.5 cm. Price, $10.00.

In reviewing a Second Edition it is always difficult to know to what extent criticism of the book as a whole is permissible. The author of this book, in his preface, states that a number of chapters have been entirely rewritten, others combined and additional ones added. Accordingly it is probably justifiable to reëxamine it as a whole. The verdict rather depends upon the attitude taken up in considering the subject. Viewed as an encyclopedic account of soil micro-organisms, their activities and interrelationship, the author's achievement is undoubtedly a brilliant one. If, however, it is to be regarded as a readable textbook, the verdict is somewhat less certain—the success of the book as such is jeopardized by the shapelessness and turgidity of some of the material presented, and the inclusion of much material not directly relevant. In other words, it lacks at times the forcefulness and strength of simplicity; its readability could be much enhanced by the ruthless use of a big blue pencil. Further, it is not at times as critical as one might wish—for example, in the discussion as to the number of organisms in the soil great prominence is given to the results of Richter, which are at variance with the generally accepted

views of many investigators in that field. As examples of the sort of material which might well have been omitted, one might mention the mathematical treatment of plate counts given on pp. 22–24. No one unacquainted with the theory of statistics could apply the data there presented, since the technical terms employed are not adequately defined, and no one wishing such knowledge would seek it in this type of book. Again, such formulas as are given on pp. 421–424, 426 and 427 for the degradation of amino acids are of very doubtful value. The table on page 597, if really necessary, might more properly have been included in the chapter on the decomposition of proteins. It is doubtful whether those sections dealing with the classification of bacteria, fungi and protozoa on pages 138, 178, 229 and 315 should really find a place in a text of this sort.

A certain amount of repetition is no doubt unavoidable in a book of this nature, and numerous instances of this can be found. The optimum P_H for the growth of fungi seems an irresistible subject. Repetition is also rather noticeable in those chapters dealing with the decomposition of plant materials, and particularly in Chapters XVI and XXIV.

The new chapters dealing with the microbiology of stable and artificial manures, of peat-bogs and forest soil, considerably enhance the value of the book. The author has stressed admirably the interrelationship of the synthetic activities of the organisms with the degradative processes carried out by them in obtaining energy. The last few chapters of the book are perhaps the most convincing; the author appears to be more at home in general discussion and broad generalization than in the more routine presentation of facts and observations.

There is no doubt that this book is of immense value to workers in soil microbiology and allied fields, and an adequate testimonial to the breadth of knowledge and vision of the author. While the publisher's statement that it is recognized as the "bible of that particular field of human enquiry" is perhaps a little generous, nevertheless it is clearly the key-book in English on soil microbiology.

GEOFFREY NORMAN

BOOKS RECEIVED

May 15, 1932–June 15, 1932

M. F. BEHAR. "Fundamentals of Instrumentation." Part One of the Manual. The Instruments Publishing Co., 3619 Forbes St., Pittsburgh, Pa. 109 pp. $2.00.

HUBERT T. S. BRITTON. "Hydrogen Ions. Their Determination and Importance in Pure and Industrial Chemistry." Second edition. D. Van Nostrand Co., Inc., 250 Fourth Ave., New York. 589 pp. $9.00.

FRIEDRICH EMICH. "Microchemical Laboratory Manual." With a Section on Spot Analysis, by Fritz Feigl. Translated by Frank Schneider. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 180 pp. $2.75.

G. FLORENCE AND J. ENSELME. "Les Problèmes de la Biochemie Moderne." Gaston Doin et Cie., Éditeurs, 8 Place de l'Odéon, Paris 6, France. 312 pp. 45 fr.

IRA D. GARRARD. "An Introduction to Organic Chemistry." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 296 pp. $3.00.

WALTHER GERLACH AND EUGEN SCHWEITZER. "Foundations and Methods of Chemical Analysis by the Emission Spectrum." Authorized Translation from the German. Adam Hilger Limited, 24 Rochester Place, Camden Road, London W. C. 1, England. 123 pp. 12/6, net; 13/0 postpaid.

M. HAISSINSKY. "L'Atomistique Moderne et la Chimie." French edition. Gaston Doin et Cie., Éditeurs, 8 Place de l'Odéon, Paris 6, France. 386 pp. 110 fr.

J. B. S. HALDANE AND KURT G. STERN. "Allgemeine Chemie der Enzyme." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 367 pp. RM. 22; bound, RM. 23.50.

B. SMITH HOPKINS. "Essentials of College Chemistry." D. C. Heath and Company, 285 Columbus Ave., Boston, Mass. 544 pp. $3.24.

JAMES MURRAY LUCK, Editor. "Annual Review of Biochemistry." Vol. I. Stanford University Press, Stanford University, Cal. 724 pp.

EDWARD G. MAHIN. "Quantitative Analysis." Fourth edition. McGraw-Hill Book Company, Inc., 330 West 42d St., New York. 623 pp. $4.00.

JOHANNES SIELISCH AND EVA GRUND. "Über den Mechanismus intra- und intermolekularer Reaktionen. Theorie des Ringtausches." Verlag Walter Blank, Derfflingerstrasse 15, Berlin W 35, Germany. 121 pp.

JOHN ARREND TIMM. "An Introduction to Chemistry. A Pandemic Text." Second edition. McGraw-Hill Book Co., Inc., 330 West 42d St., New York. 553 pp. $3.50.

FRANK C. WHITMORE, Editor-in-Chief. "Organic Syntheses." Vol. XII. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 96 pp. $1.75.

"The Adsorption of Gases by Solids." A General Discussion Held by The Faraday Society, January, 1932. Gurney and Jackson, 33 Paternoster Row, London E. C., 4, England. 128 pp. 15/-.

"Annual Survey of American Chemistry." Vol. VI, 1931. Edited by Clarence J. West. Published for the National Research Council by The Chemical Catalog Company, Inc., 419 Fourth Ave., New York. 573 pp. $4.50.

"The Scientific Journal of the Royal College of Science." Vol. II. Edward Arnold and Co., 41–43 Maddox St., London W. 1, England. 162 pp. 7s./6d.

The Journal of the American Chemical Society

VOL. 54 AUGUST, 1932 No. 8

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE CALCULATION OF PARTIAL MOLAL QUANTITIES

BY T. F. YOUNG AND O. G. VOGEL

RECEIVED JANUARY 25, 1932 PUBLISHED AUGUST 5, 1932

For many applications of thermodynamics to chemical and physical problems it is necessary to employ the partial derivative, with respect to the amount of some substance present, of an extensive[1] quantity G, such as the volume, entropy, heat capacity, etc. The role of such quantities in the thermodynamics of mixtures has been discussed by Lewis.[2] The partial derivative of G with respect to the number of moles, n_1, of the constituent designated as number one is termed by Lewis and Randall[3] the "partial molal" property of that constituent. They represent it by the symbol $\bar{G}_1$, thus

$$\bar{G}_1 \equiv \left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3 \cdots P, T}$$

The subscripts indicate that the number of moles of each of the constituents other than number one are held or "considered held" constant, and likewise that the pressure, P, and the temperature, T, are considered constant; in other words, P, T and the amounts of each of the constituents are selected as independent variables.

Several methods for the calculation of partial molal quantities have been discussed by Lewis and Randall. They have described two methods which involve certain intensive properties rather than the extensive ones embodied in the fundamental definition of $\bar{G}$. More recently, Sosnick[4] and Randall and Rossini[5] have suggested other similar procedures which are very useful.

As pointed out by these authors, appropriate changes of variables are frequently very convenient. They permit the use of curves with finite

[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 13.

[2] Lewis, *Proc. Am. Acad.*, **43**, 259 (1907), especially p. 273.

[3] (a) Lewis and Randall, THIS JOURNAL, **43**, 233 (1921); (b) Ref. 1, Chapter IV.

[4] Sosnick, THIS JOURNAL, **49**, 2255 (1927).

[5] Randall and Rossini, *ibid.*, **51**, 323 (1929).

slopes in critical regions, or curves which follow closely, simple empirical equations. Plots of small deviations from such equations can often be manipulated with less effort or more accuracy than the plot of the complete function. A change of variables sometimes aids also in the utilization of data already available in a particular form.

To facilitate changes of variables, two tables have been prepared in this Laboratory which exhibit the relations between a number of common intensive properties, various composition terms, and the corresponding partial molal quantities. These tables are useful aids in the selection and manipulation of convenient functions.

The mathematical methods employed in the construction of the tables are simple and well known. A single illustration will suffice: $\bar{G}_1$ is to be obtained from a plot of $y = \mathbf{G}/(n_1 + n_2)$ against N_1, the mole fraction of constituent number one. For example, G might represent volume, and y the volume of one mole of solution.

$$(\partial y)_{n_2,\,P,\,T} = \frac{(\partial \mathbf{G})_{n_2,\,P,\,T}}{(n_1 + n_2)} - \frac{\mathbf{G}}{(n_1 + n_2)^2}(\partial n_1)_{n_2,\,P,\,T} \tag{1}$$

$$(\partial \mathbf{G})_{n_2,\,P,\,T} = (n_1 + n_2)(\partial y)_{n_2,\,P,\,T} + y(\partial n_1)_{n_2,\,P,\,T} \tag{2}$$

The mole fraction $N_1 = \dfrac{n_1}{n_1 + n_2}$

$$(\partial N_1)_{n_2\,P,\,T} = \frac{1}{(n_1 + n_2)}(\partial n_1)_{n_2,\,P,\,T} - \frac{n_1(\partial n_1)_{n_2,\,P,\,T}}{(n_1 + n_2)^2} \tag{3}$$

$$(\partial n_1)_{n_2,\,P,\,T} = \frac{n_1 + n_2}{N_2}(\partial N_1)_{n_2,\,P,\,T} \tag{4}$$

$$\bar{G}_1 = N_2\left(\frac{\partial y}{\partial N_1}\right)_{n_2,\,P,\,T} + y = N_2\left(\frac{\partial y}{\partial N_1}\right)_{P,\,T} + y \tag{5}$$

The subscript n_2 may be omitted since the value of $\mathrm{d}y/\mathrm{d}N_1$ is obviously independent of the way in which N_1 is varied at constant pressure and temperature. This formula corresponds to the one in Table I

$$\bar{G}_1 = N_2 S + y - C \tag{6}$$

for the special case in which $C = 0$. S represents the slope of the curve.

Symbols

W_1 and W_2 = mass of one mole of constituents 1 and 2, respectively
n_1 and n_2 = numbers of moles of constituents 1 and 2, respectively
N_1 and N_2 = mole fractions of constituents 1 and 2
$r_1 = n_1/n_2$; $r_2 = n_2/n_1 = m\ W_1/1000$
m = moles of constituent 2 (solute) per 1000 g. of constituent 1 (solvent)
G = any extensive property of the mixture consisting of n_1 moles of constituent 1 and n_2 moles of 2
G_1 and G_2 = molal properties of pure constituents 1 and 2
$\Phi = (\mathbf{G} - n_1 G_1)/n_2$, apparent molal property of constituent 2
$G = \mathbf{G}/(n_1 + n_2)$
$\Delta = G - (N_1 G_1 + N_2 G_2)$

TABLE I

FORMULAS FOR THE CALCULATION OF $\overline{G}_1$

	x 1	2	3	4
	y	N_1	N_2	m	$m^{1/2}$
A	$\frac{G}{n_2} + C$	$N_2^2 S$	$-N_2^2 S$	$-\frac{mS}{r_1}$	$-\frac{m^{1/2}S}{2r_1}$
B	$\frac{G}{n_1 + n_2} + C$	$N_2 S + y - C$	$-N_2 S + y - C$	$-\frac{mS}{N_1} + y - C$	$-\frac{m^{1/2}S}{2N_1} + y - C$
C	$\frac{n_1 + n_2}{G} + C$	$-\frac{N_2 S}{(y-C)^2} + \frac{1}{y-C}$	$\frac{N_2 S}{(y-C)^2} + \frac{1}{y-C}$	$\frac{mS}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{m^{1/2}S}{2N_1(y-C)^2} + \frac{1}{y-C}$
D	$\Phi + C$	$G_1 + N_2^2 S$	$G_1 - N_2^2 S$	$G_1 - \frac{mS}{r_1}$	$G_1 - \frac{m^{1/2}S}{2r_1}$
E	Δ	$G_1 + y + N_2 S$	$G_1 + y - N_2 S$	$G_1 + y - \frac{mS}{N_1}$	$G_1 + y - \frac{m^{1/2}S}{2N_1}$
F	G_W	$W_1\left[y + \left(N_1 N_2 + \frac{N_2^2 W_2}{W_1}\right)S\right]$	$W_1\left[y - \left(N_1 N_2 + \frac{N_2^2 W_2}{W_1}\right)S\right]$	$W_1\left[y - \left(m + \frac{W_2 m^2}{1000}\right)S\right]$	$W_1\left[y - \left(\frac{m^{1/2}}{2} + \frac{m^{3/2}W_2}{2000}\right)S\right]$

	x 5	6	7	8
	y	m^k	$\log_{10}(m^k)$	r_2	r_1
A	$\frac{G}{n_2} + C$	$-\frac{km^k S}{r_1}$	$-\frac{kS}{2{,}303\, r_1}$	$-r_2^2 S$	S
B	$\frac{G}{n_1 + n_2} + C$	$-\frac{km^k S}{N_1} + y - C$	$-\frac{kS}{2.303\, N_1} + y - C$	$-\frac{r_2 S}{N_1} + y - C$	$\frac{S}{N_2} + y - C$
C	$\frac{n_1 + n_2}{G} + C$	$\frac{km^k S}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{kS}{2.303 N_1 (y-C)^2} + \frac{1}{y-C}$	$\frac{r_2 S}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{-S}{N_2(y-C)^2} + \frac{1}{y-C}$
D	$\Phi + C$	$G_1 - \frac{km^k S}{r_1}$	$G_1 - \frac{kS}{2.303 r_1}$	$G_1 - r_2^2 S$	$G_1 + S$
E	Δ	$G_1 + y - \frac{km^k S}{N_1}$	$G_1 + y - \frac{kS}{2.303\, N_1}$	$G_1 + y - \frac{r_2 S}{N_1}$	$G_1 + y + \frac{S}{N_2}$
F	G_W	$W_1\left[y - \left(km^k + \frac{kW_2 m^{k+1}}{1000}\right)S\right]$	$W_1\left[y - \frac{k}{2.303}\left(1 + \frac{W_2 m}{1000}\right)S\right]$	$W_1\left[y - \left(r_2 + \frac{r_2^2 W_2}{W_1}\right)S\right]$	$W_1\left[y + \left(r_1 + \frac{W_2}{W_1}\right)S\right]$

TABLE II

FORMULAS FOR THE CALCULATION OF G_2

	y	x 1 N_1	2 N_2	3 m	4 $m^{1/2}$
A	$\frac{G}{n_2} + C$	$-N_1N_2S + y - C$	$N_1N_2S + y - C$	$mS + y - C$	$\frac{m^{1/2}S}{2} + y - C$
B	$\frac{G}{n_1 + n_2} + C$	$-N_1S + y - C$	$N_1S + y - C$	$\frac{mS}{N_2} + y - C$	$\frac{m^{1/2}S}{2N_2} + y - C$
C	$\frac{n_1 + n_2}{G} + C$	$\frac{N_1S}{(y-C)^2} + \frac{1}{y-C}$	$-\frac{N_1S}{(y-C)^2} + \frac{1}{y-C}$	$-\frac{mS}{N_2(y-C)^2} + \frac{1}{y-C}$	$-\frac{m^{1/2}S}{2N_2(y-C)^2} + \frac{1}{y-C}$
D	$\Phi + C$	$-N_1N_2S + y - C$	$N_1N_2S + y - C$	$mS + y - C$	$\frac{m^{1/2}S}{2} + y - C$
E	Δ	$G_2 + y - N_1S$	$G_2 + y + N_1S$	$G_2 + y + \frac{mS}{N_2}$	$G_2 + y + \frac{m^{1/2}S}{2N_2}$
F	G_w	$W_2\left[y - \left(N_1N_2 + \frac{N_1^2W_1}{W_2}\right)S\right]$	$W_2\left[y + \left(N_1N_2 + \frac{N_1^2W_1}{W_2}\right)S\right]$	$W_2\left[y + \left(m + \frac{1000}{W_2}\right)S\right]$	$W_2\left[y + \left(\frac{1000}{2m^{1/2}W_2} + \frac{m^{1/2}}{2}\right)S\right]$

	y	x 5 m^k	6 $\log_{10}(m^k)$	7 r_2	8 r_1
A	$\frac{G}{n_2} + C$	$km^kS + y - C$	$\frac{kS}{2.303} + y - C$	$r_2S + y - C$	$-r_1S + y - C$
B	$\frac{G}{n_1 + n_2} + C$	$\frac{km^kS}{N_2} + y - C$	$\frac{kS}{2.303\,N_2} + y - C$	$\frac{S}{N_1} + y - C$	$-\frac{r_1S}{N_2} + y - C$
C	$\frac{n_1 + n_2}{G} + C$	$-\frac{km^kS}{N_2(y-C)^2} + \frac{1}{y-C}$	$-\frac{kS}{2.303N_2(y-C)^2} + \frac{1}{y-C}$	$-\frac{S}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{r_1S}{N_2(y-C)^2} + \frac{1}{y-C}$
D	$\Phi + C$	$km^kS + y - C$	$\frac{kS}{2.303} + y - C$	$r_2S + y - C$	$-r_1S + y - C$
E	Δ	$G_2 + y + \frac{km^kS}{N_2}$	$G_2 + y + \frac{kS}{2.303\,N_2}$	$G_2 + y + \frac{S}{N_1}$	$G_2 + y - \frac{r_1S}{N_2}$
F	G_w	$W_2\left[y + \left(\frac{1000km^{k-1}}{W_2} + km^k\right)S\right]$	$W_2\left[y + \frac{k}{2.303}\left(1 + \frac{1000}{mW_2}\right)S\right]$	$W_2\left[y + \left(\frac{W_1}{W_2} + r_2\right)S\right]$	$W_2\left[y - \left(\frac{r_1^2W_1}{W_2} + r_1\right)S\right]$

$G_w = G/(n_1W_1 + n_2W_2)$, specific property (*i. e.*, specific heat, etc.)

$$\overline{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2}; \quad \overline{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n_1}$$

C = any constant
k = any exponent
y = the quantity plotted as ordinate
x = the quantity plotted as abscissa
S = the slope of the curve = dy/dx

The units of quantity chosen for the formulas placed above the double lines are purely arbitrary and may be varied at will. Thus W_1' may represent any desirable amount of constituent 1, and W_2' a convenient quantity of constituent 2. Then n_1' and n_2' will represent the numbers of such units and r_2' the ratio of the numbers of units of constituent 2 to the number of units of constituent 1. Except for the addition of primes to each symbol, the same formulas will represent the partial derivatives for the quantities corresponding to W_1' and W_2'. For example if W_1' represents one gram, $\overline{G}_1'$ represents a partial specific property and must be multiplied by the molal weight of the first constituent to yield a partial molal quantity.

It is sometimes convenient to plot such quantities as heat capacity *per gram* against *mole* (rather than weight) fraction. Below the double lines in the tables are a few formulas arranged for direct calculation of partial molal properties from such typical pairs of dissimilar units.

Some of these formulas have already been used or suggested. 1-E is the relation recommended by Sosnick.[4] It is especially useful in those cases in which Δ is very small. 1-C is the basis of the method of intercepts used by Lewis and Randall,[3] 6-D was also used by Lewis and Randall, and 4-D without the constant, was employed by Randall and Rossini.

The list presented is, of course, not complete but contains the formulas which seem to us most likely to be useful. If special problems require other relations, those presented here are sufficiently varied to act as guides in the selection of other formulas which might be of value.

Summary

Formulas have been prepared to facilitate changes of variables in the calculation of partial molal properties of the constituents of solutions. These are presented in tables.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE RELATIVE HEAT CONTENTS OF THE CONSTITUENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

BY T. F. YOUNG ANG O. G. VOGEL

RECEIVED JANUARY 25, 1932 PUBLISHED AUGUST 5, 1932

The complete evaluation of activity coefficients from freezing point measurements is dependent upon the determination of relative partial molal heat contents. The data available for their evaluation are neither as extensive nor as accurate as desirable. In this paper are presented an examination of previously published data for aqueous sodium chloride solutions at 25°, a few new experimental determinations, a convenient method for utilizing a combination of heat of solution and heat of dilution data, and finally the results of new calculations.

The data first employed for the evaluation of relative partial molal heat contents of sodium chloride were those of Randall and Bisson.[1] They measured a series of heats of dilution from about 6.1 *m* to 0.41 *m* and the heat of solution of sodium chloride in sufficient water to produce compositions between 0.13 *m* and 0.54 *m*. Later Wüst and Lange[2] measured heats of solution between 0.43 *m* and 5.6 *m* and with a few heats of dilution extended their data to about 6.1 *m*. More recently Lipsett, Johnson and Maass[3] determined many heats of solution at both 20 and 25°. They made one dilution between 0.173 *m* and 0.0284 *m*.

Because the work of Randall and Bisson and that of Wüst and Lange were not extended to sufficiently dilute solutions, a change in sign of the heat of dilution was not revealed. Later Lipsett, Johnson and Maass, and Lange and Messner,[4] observed that heat was evolved by the dilution of a very dilute solution of sodium chloride at 25°. Several years earlier Pratt[5] had observed similar behavior of several electrolytes. His curves for sodium chloride exhibit evidence of the reversal phenomenon.

Examination and Treatment of Previous Data.—For comparison, the three series of heat of solution data were represented by separate plots. The *experimental* values reported in the first paper of Lipsett, Johnson

[1] Randall and Bisson, THIS JOURNAL, **42**, 347 (1920).

[2] Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

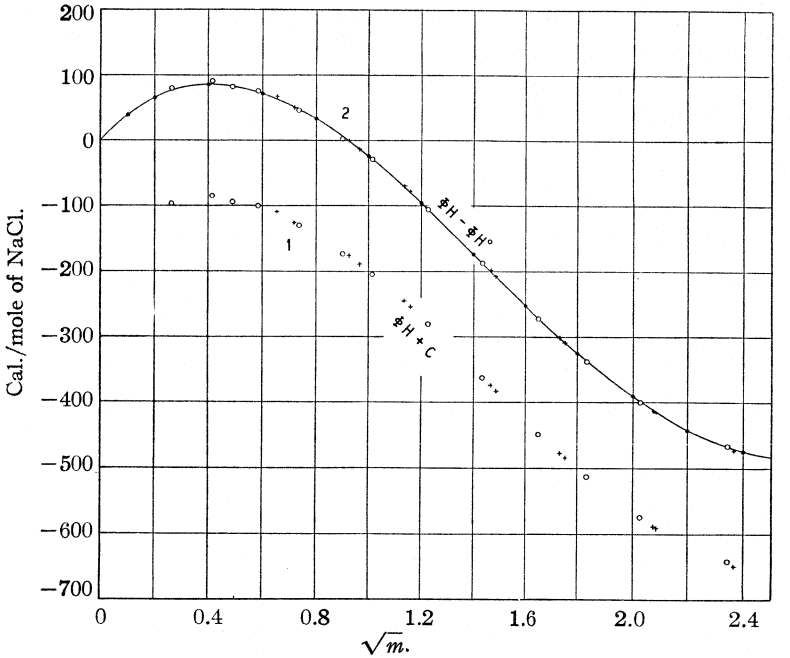
[3] (a) Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 925 (1927); (b) **49**, 1940 (1927).

[4] (a) Lange and Messner, *Naturwissenschaften*, **15**, 521 (1927); (b) *Z. Elektrochem.*, **33**, 431 (1927).

[5] Pratt, *J. Franklin Inst.*, **185**, 663 (1918); *cf.* Thomsen, "Thermochemistry," Longmans, Green and Co., London, 1908, p. 178. Thomsen reported evolution of heat for the dilution of his 0.28 *m* solution, but the results of modern workers indicate that the opposite effect should have been observed.

and Maass were multiplied by 0.9995 to correct them in accordance with the second report of these authors and to convert them to 15° calories.

The experiments of Wüst and Lange and of Lipsett, Johnson and Maass were first compared. The difference between the two series was nearly constant. Since absolute values are not required for the determination of relative partial molal properties, one curve was superimposed upon the other and adjusted until the two appeared to be as nearly coincident as the data would permit. Appropriate constants, one of which was entirely arbitrary, were then added to the data in each series so that they could be represented on one plot. Curve 1 (indicated only) of Fig. 1 exhibits the satisfactory agreement of the relative values obtained from the two series.



+, Wüst and Lange; ○, Lipsett, Johnson and Maass; ●, $\int S dm^{1/2}$.

Fig. 1.—Curve 1 (indicated) represents experimental determinations of the heat absorbed during the solution of one mole of sodium chloride, plus an arbitrary constant; the data are those of Lipsett, Johnson and Maass plus a convenient constant, −1100, and those of Wüst and Lange, −1108. Curve 2, $\phi H - \phi H^\circ$ as determined by integration of the S curve, Fig. 2, plotted with the data of Lipsett, Johnson and Maass −924 and those of Wüst and Lange −932.

The heat of solution data calculated by Randall and Bisson were very different from the others, but that portion of their curve corresponding to the composition range in which they actually made solution experiments

is in good agreement with the measurements of Wüst and Lange. These data will be discussed after the significance and use of the curve has been considered.

The heat absorbed during the solution of one mole of sodium chloride, ΔH, differs from the apparent molal heat content, ϕH, by the heat content of one mole of solid sodium chloride, H_2

$$\phi H = \Delta H + H_2 \qquad (1)$$

Curve 1, Fig. 1, therefore represents the apparent molal heat content plus a constant, C.

The $\sqrt{m}$ was chosen as abscissa in Fig. 1, so that the slope of the curve would approach a finite value as m approaches zero. Investigations of the solubilities of salts in very dilute aqueous solutions of other salts have demonstrated that the activity coefficients, γ, of many strong electrolytes are nearly linear functions of $\sqrt{m}$ in very dilute solutions, and that $d\gamma/d\sqrt{m}$ approaches a finite limit as m approaches zero. For this to be true at more than one temperature $d(\phi H)/d\sqrt{m}$ must approach either zero or a finite value. Randall and Rossini's[6] heat capacity measurements of sodium chloride solutions have established that this slope has a temperature coefficient and cannot in general be zero.

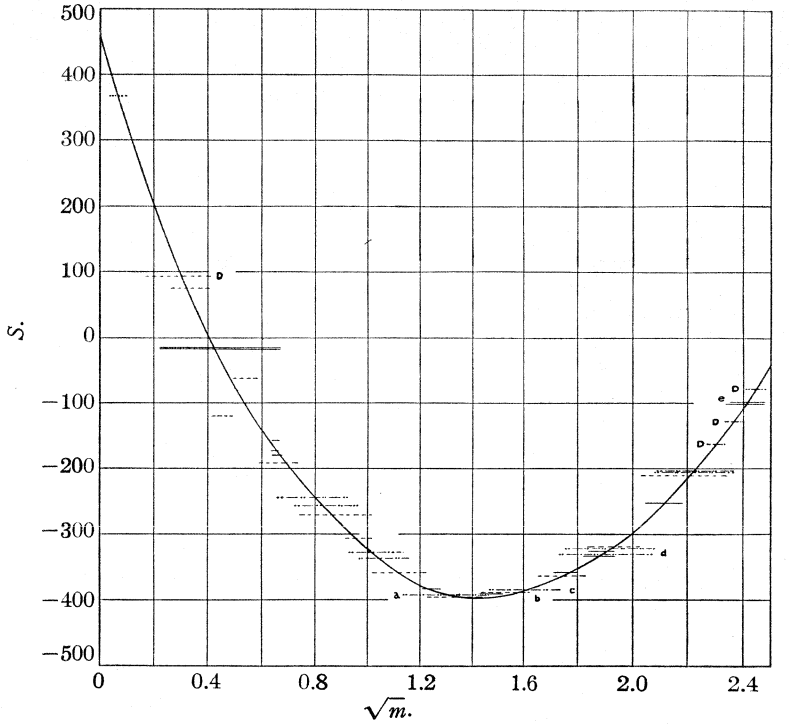
The Derivative Curve.—Customary graphical methods of differentiation are not convenient for the precise manipulation of both heat of solution and heat of dilution data. Figure 2 illustrates the method employed for determination of the slope, $S \equiv d(\phi H)/d\sqrt{m}$, of Curve 1, Fig. 1. Between any two values of $\sqrt{m}$, the average of the slope is $\Delta(\phi H)/\Delta\sqrt{m}$. The value of $\Delta(\phi H)$ may be calculated directly from the heat of dilution of one mole of sodium chloride or from the difference in two heats of solution. The average values of the slope, S, are equal to the slopes of chords between corresponding points of Curve 1, Fig. 1.

Average values of S were determined from all of the data in the two series represented on Curve 1 and from one dilution experiment of Lange and Messner. These were plotted as lines drawn between corresponding values of $\sqrt{m}$. The true derivative curve should pass through each chord so that the two areas enclosed between the curve, the chord and imaginary vertical lines drawn through the ends of the chord, are equal.

Comparison of chords revealed the source of differences between the data reported by Randall and Bisson and by subsequent workers. The chords calculated from Randall and Bisson's measurements fell erratically on both sides of the curve, Fig. 2. The errors of several dilution experiments accumulated and affected the estimated form of their heat of solution curve. As a result, heat of solution data tabulated by those authors for large values of m are in error whereas actual solution measurements and

[6] Randall and Rossini, THIS JOURNAL, 51, 323 (1929).

the corresponding tabulations for dilute solutions agree well with the data of Wüst and Lange.



·· — ·· — ··, Wüst and Lange; ....., Lange and Messner; – – – – –, Lipsett, Johnson and Maass; ————, Young and Vogel.

Fig. 2.—The curve represents $S = d(\phi H)/d\sqrt{m}$. Each horizontal line represents an experimental determination of $\Delta(\phi H)/\Delta\sqrt{m}$ through the range indicated by the terminal abscissas of the line. The data of Lange and Messner and of Young and Vogel were obtained from dilution experiments. Most of the chords calculated from the work of Wüst and Lange and of Lipsett, Johnson and Maass represent differences in heats of solution. The few obtained from dilution measurements are distinguished by a symbol, D. Two chords of Wüst and Lange were omitted from the plot because they were nearly coincident with others designated, respectively, a and c. Similarly, chords of Young and Vogel were omitted because of proximity to those marked a, b, c and e. Two were omitted at d.

Since chords calculated from the early work of Randall and Bisson could not aid in locating the derivative curve, they were not added to the plot, Fig. 2. This somewhat arbitrary procedure required further justification. Furthermore in certain regions of the graph additional chords were desirable. Because heats of dilution yield directly the desired average slopes, they were determined experimentally.

Experimental Procedure

The calorimeter is illustrated in Fig. 3. A silvered Dewar flask, D, of about one liter capacity was cemented with litharge and glycerin to a metal ring, R, to which was bolted the calorimeter cap, F. This cap was provided with five vertical tubes, one for each of the following: a stirrer, S; a heater, H; a thermel, T; a bulb, B; and a bulb crushing device, C. Each tube was equipped with a tight-fitting rubber tube, cotton packing moistened with oil, or with an oil seal. Corrosion was prevented by a coating of paraffin on various metal parts.

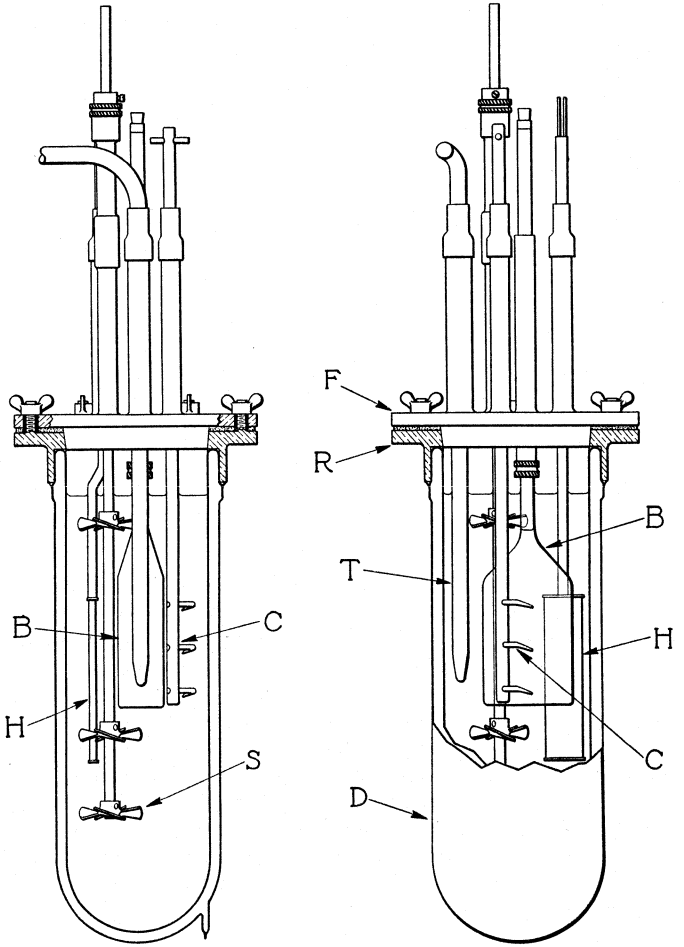


Fig. 3.—The calorimeter.

The bulbs were very thin-walled Pyrex glass vessels of 75–85 cc. capacity. During each dilution experiment, a bulb was broken by the manual rotation of the crushing device. The heat produced by the mixing process was measured several times. When there was water both inside and outside the bulb, about 0.07 calorie was produced. This corresponds to a temperature rise of about 0.00009°.

The stirrer was driven at about 500 revolutions per minute by a synchronous motor. Before each dilution the temperature of the liquid in the calorimeter was allowed to become practically constant. The equilibrium attained was about 0.2° above the surroundings.

The core of the calorimeter heater was a mica strip wound with constantan wire. It was enclosed in a tight-fitting metal sheath separated from the core by thin sheets of mica.

Current was supplied by a large storage battery. For several minutes before it was used, it was permitted to discharge through a coil, the resistance of which was nearly equal to that of the heater. During a customary three-minute heating interval the current, of about 0.04 ampere, varied but a few hundredths of one per cent.

Current was determined during each heating period from a measurement of the potential drop across a standard 0.1-ohm resistance. The length of the period was measured by a stop watch which had been compared with an accurate clock.

One or more heating periods (usually two) followed each mixing process. When a steady cooling rate had been established after the final period, current was again allowed to flow through the heater and was measured as before. With the potentiometer and standard 1 and 10,000 ohm resistances, the potential drop across the heater was also determined. These measurements revealed a variation, throughout the whole work, of only about 0.03% in the resistance of the heater.

Two copper–constantan thermels were constructed in accordance with many of the recommendations of White.[7] Because they were used principally for the determination of the ratio of successive temperature changes, great care in calibration and in several details of construction was not essential. Comparison with a mercury thermometer calibrated by the Bureau of Standards was sufficient for the determination of the temperature of the calorimeter contents. One of the thermels which contained twenty-four pairs of wires produced a galvanometer deflection somewhat greater than one centimeter per microvolt. The precision of reading was about 0.02 microvolt, corresponding to approximately 0.00002°. One end of the thermel dipped into the calorimeter, the other into a silvered Dewar bulb which was placed near the calorimeter in a thermostat.

The thermostat was controlled by a large mercury regulator. Its precision was investigated with a thermel, one end of which was immersed as usual in its Dewar bulb. The other end was exposed directly to the thermostat. No fluctuations greater than two thousandths of a degree were detected over periods of many minutes. Inside the calorimeter, fluctuations were very much smaller.

The e. m. f. produced by the thermel was determined each minute during the periods preceding the breaking of the bulb and before and after each heating interval. These values were plotted as functions of time and the appropriate linear portions of the plot were extrapolated to lines representing, respectively, the instant of breaking the bulb, and the center of each electrical heating period. From the plot, the e. m. f. change produced by each operation was ascertained. More elaborate methods for the estimation of thermal leakage were not justified.

The electrical energy required for an increase of one volt in the thermel e. m. f. was computed for each heating interval. There was no significant variation in successive values of this ratio. The heat of mixing was computed by multiplying this ratio, calories/volt, by the change in thermel e. m. f. produced by the mixing process.

Materials.—Concentrated solutions were prepared from fused sodium chloride and distilled water. They were analyzed gravimetrically, some by silver chloride precipitation, others by sodium chloride residue methods. In the latter determinations

[7] White, THIS JOURNAL, **36**, 2292 (1914).

high temperatures were used in accordance with the observations of Richards and Hall.[8] Dilute solutions were prepared by the dilution of a stock solution about 5.5 molal.

Experimental Results and Calculations

The small temperature changes produced precluded any attempt with available equipment to obtain a precision much better than one or two in a hundred. The dilution of solutions about 0.45 molal produced lowerings of only about 0.0002°. Nevertheless the average deviation from the mean of three such experiments represented an error in temperature measurement of only about 0.00002°. The precision of the experiments with concentrated solutions was limited by analytical methods. Because of the rapid variation of the slope, S, with concentration, an error of 0.1% in the analysis of a 6.1 m solution of sodium chloride would correspond to an error of about 1% in the measured value of the chord.

The experimental results are in Table I. The first and second columns exhibit the initial and final values of the molality. The third column shows the temperature of the calorimeter contents before mixing and the fourth the approximate rise in temperature due to the mixing operation. The fifth contains $\Delta(\phi H)$, which is the heat (15° calorie) which would be absorbed per mole of sodium chloride in an isothermal dilution process at the temperature stated in the third column. In the sixth column is the value of $\Delta(\phi H)$ calculated for 25°. The last column contains the chord for use in the determination of the S curve.

TABLE I

$\sqrt{m_1}$	$\sqrt{m_2}$	t, °C.	Δt, °C.	$\Delta\phi H_t$	$\Delta\phi H_{25°}$	$\Delta\phi H/\Delta\sqrt{m}$
0.670	0.215	24.93	−0.0003	7.7	7.2	− 16
.670	.219	24.93	− .0003	8.2	7.8	− 17
.6645	.6328	24.97	− .002	5.07	5.06	−160
.6641	.6307	24.93	− .002	5.81	5.78	−173
.6719	.6374	24.94	− .002	6.23	6.20	−180
1.2769	1.2071	24.96	− .04	26.77	26.73	−383
1.4791	1.4063	25.04	− .05	28.60	28.64	−393
1.5168	1.4282	25.06	− .07	34.52	34.59	−390
1.6254	1.5382	25.02	− .08	33.87	33.89	−389
1.6248	1.5364	25.02	− .08	34.00	34.02	−385
1.7991	1.7110	24.99	− .09	31.55	31.54	−358
1.9365	1.8199	25.21	− .12	38.51	38.85	−333
1.9365	1.8319	25.27	− .11	34.19	34.57	−331
1.9365	1.8338	25.16	− .11	33.73	33.96	−331
1.9365	1.8374	25.32	− .10	31.93	32.36	−326
2.1758	2.0432	25.07	− .13	33.36	33.46	−252
2.4789	2.3377	25.33	− .07	13.68	14.22	−100.7
2.4789	2.3488	25.31	− .06	12.27	12.76	− 98.0
2.4789	2.3522	25.09	− .06	12.17	12.31	− 97.1

[8] Richards and Hall, THIS JOURNAL, **51**, 709 (1929).

The value of $\Delta(\phi H)$ at 25° (column 6) was calculated from the corresponding quantity at the temperature of observation by means of the apparent molal heat capacity, ϕC, which is the temperature coefficient of ϕH.

$$\phi C = \mathrm{d}(\phi H)/\mathrm{d}T \qquad \Delta(\phi C) = \mathrm{d}(\Delta(\phi H)/\mathrm{d}T) \tag{2}$$

For the purpose of the calculation,[9] a plot was prepared of ϕC *versus* $\sqrt{m}$. The data of Randall and Rossini were supplemented by ϕC data calculated from differences in the heats of solution determined by Lipsett, Johnson and Maass for 20 and 25°. Though these values of ϕC were merely averages for the five degree interval, they were sufficient for a satisfactory extension of the 25° curve.

Final Construction of Differential Curve.—After the new data had been added to the plot, a preliminary curve was carefully drawn in accordance with all of the chords. The curve was then tested and slightly readjusted as follows: the first derivative of the preliminary S curve was determined at numerous values of $\sqrt{m}$. For this purpose the tangentometer described by E. v. Harbou[10] was used. From a plot of S' the next higher derivative, S'', was estimated. When S'' may be considered constant over the range covered by any chord, the following equation may be used for the calculation of the difference between P, a point on the curve directly above the center of any chord, and $\bar{P}$, the ordinate of the chord itself.

$$P - \bar{P} = -(\mathrm{S}''/24)(\Delta\sqrt{m})^2 \tag{3}$$

Values of P were calculated for all of the chords and were plotted on a large graph. Since each chord was represented by a point, all of the data could be placed, without conflict, upon a single sheet of paper, and it was less difficult to draw the S curve with due regard to all of the data than on the original chord plot. The new diagram served as a convenient aid for testing and improving the fundamental chord plot.

Further confirmation of Fig. 2 in the region between $\sqrt{m} = 0.4$ and 1.5 was obtained from the work of Richards and Rowe, who determined a few heats of dilution at approximately 15 and 20°. Chords for 25°, calculated from their 20° data by means of values of ϕC, read from a curve similar to that discussed above,[11] are in satisfactory agreement with the data represented in Fig. 2.

The position of the S curve in the neighborhood of $\sqrt{m} = 0.05$ was largely determined by a measurement made by Lange and Messner. Except for the portion to the left of that chord, the curve seems to be sufficiently precise for application to thermodynamic problems.

[9] *Cf.* Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

[10] Harbou, *Z. angew. math. Mechanik*, **10**, No. 6 (1930).

[11] This curve, determined from the measurements of Lipsett, Johnson and Maass, represented average values of ϕC between 20 and 25°.

Extrapolation into the region of great dilution is, of course, uncertain.[12] However, an error as large as 200 in the estimated average value of S between $\sqrt{m} = 0$ and 0.05 would introduce an error of only 10 cal./mole into calculations of ϕH.

Column 2 of Table II contains values of S read from the large plot. The curve between $\sqrt{m} = 0$ and 0.4 is well represented by the following empirical equation[13]

$$S = 461.3 - 1427.6\sqrt{m} + 704.2\,m \qquad (4)$$

TABLE II

$\sqrt{m}$	S	$\phi H - \phi H^\circ$	$\bar{L}_1$	$\bar{L}_2$
0.05	392	21	−0.0004	31
.1	325	39	− .0029	56
.15	263	54	− .008	74
.2	204	66	− .015	86
.3	96	81	− .023	95
.4	3	85	− .002	86
.5	− 76	82	+ .086	63
.6	−141	71	.27	29
.7	−196	54	.61	− 14
.8	−244	32	1.13	− 65
.9	−286	6	1.88	−123
1.0	−322	− 25	2.90	−186
1.2	−377	− 95	5.9	−321
1.4	−398	−173	9.8	−452
1.6	−386	−252	14.2	−561
1.8	−352	−326	18.5	−643
2.0	−297	−391	21.4	−688
2.1	−259	−419	21.6	−691
2.2	−215	−443	20.6	−679
2.4	−108	−475	13.5	−605
2.45	− 76	−480	10.1	−573

In the third column of Table II are values of the differences between ϕH, the apparent molal heat content, and ϕH°, the limit approached by

[12] For a summary of the important investigations of this problem by Lange and his co-workers, see Lange and Robinson, *Chemical Reviews*, 9, 89 (1931). See also Robinson, THIS JOURNAL, **54**, 1311 (1932). At the time this paper was written the precise data of Robinson had not been published. Chords calculated from his measurements are in good agreement with Fig. 2 and contribute greatly to the reliability of extrapolation.

[13] According to the theory of Debye and Hückel $dS/d\sqrt{m}$ is related to ionic size [see Bjerrum, *Trans. Faraday Soc.*, **23**, 445 (1927), Equation 4]. From the second derivative, with respect to $\sqrt{m}$, of Bjerrum's equation 4, an expression was easily obtained for the limit of $dS/d\sqrt{m}$ as $\sqrt{m} \doteq 0$. This was equated to a numerical value derived from equation (4). According to the resulting relation, the mean effective ionic diameter is 4.7×10^{-8} cm. This is the expected order of magnitude in spite of certain approximations in Bjerrum's equation. If theory can be used as a guide, our extrapolation is probably not far from correct.

ϕH as $\sqrt{m}$ approaches 0. These tabulated values of $\phi H - \phi H^\circ$ were obtained from the equation

$$\phi H - \phi H^\circ = \int_0^{\sqrt{m}} S \mathrm{d}\sqrt{m} \qquad (5)$$

For $\sqrt{m} < 0.4$ this becomes

$$\phi H - \phi H^\circ = 461.3\, m^{1/2} - 713.8\, m + 235\, m^{3/2} \qquad (6)$$

Mechanical integration was employed for the determination of values of $\phi H - \phi H^\circ$ which were not calculated from equation 6.

The Integral Curve.—A plot of $\phi H - \phi H^\circ$ was constructed and compared with the curve representing the heat of solution data of Lipsett, Johnson and Maass. The latter curve, according to Equation 1, represents $\phi H - H_2$. The difference in the ordinates of the two curves is therefore $\phi H^\circ - H_2$, which is the heat absorbed during the solution of one mole of sodium chloride in an infinite amount of water. One curve was placed over the other and shifted until the two were as nearly coincident as possible. From the amount of the shift, $\phi H - H_2$ was determined as 924. In a similar manner Wüst and Lange's data yielded 932.

From each of the two series of experimental data, values of $\phi H - \phi H^\circ$ were calculated by subtraction of these respective constants. They were compared on Curve 2, Fig. 1, with the direct results of the integration of the S curve.

The Relative Heat Contents.—According to Lewis and Randall's convention[14] the difference between $\overline{H}$, the partial molal heat content of any constituent and $\overline{H}^\circ$, the partial molal heat content of that substance in its reference state, is termed the "Relative Heat Content."

When the infinitely dilute solution is chosen as the reference state of both constituents, the relative heat content of the solvent, $\overline{L}_1$, and of the solute, $\overline{L}_2$, may be calculated from the following equations, 7 and 8. These are easily obtained from formulas 4-D of each of the tables in the preceding paper.

$$\overline{L}_1 = \overline{H}_1 - \overline{H}^\circ_1 = -\frac{m^{3/2}\mathrm{S}}{2(55.51)} \qquad (7)$$

$$\overline{L}_2 = \overline{H}_2 - \overline{H}^\circ_2 = \phi H - \phi H^\circ + \frac{m^{1/2} S}{2} \qquad (8)$$

Combinations of these with equations 4 and 6 give 9 and 10, valid for values of the $\sqrt{m}$ less than 0.4.

$$\overline{L}_1 = -4.16\, m^{3/2} + 12.86\, m^2 - 6.34\, m^{5/2} \qquad (9)$$

$$\overline{L}_2 = 692\, m^{1/2} - 1428\, m + 587\, m^{3/2} \qquad (10)$$

The new determinations of $\overline{L}_1$ and $\overline{L}_2$ are exhibited in Table II.[15] Those corresponding to values of $\sqrt{m} < 0.4$ were computed from equations 9

[14] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, 1923, pp. 351 and 354.

[15] For similar tables of properties of dilute solutions of sodium chloride at 18° see Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

and 10. The others are the results of substitution in equations 7 and 8 of the data listed in Columns 2 and 3.

Lewis and Randall's[16] calculations of the activity coefficients of sodium chloride depended upon the classic $\overline{L}_1$ data of Randall and Bisson. The data of Table II, together with the new heat capacity data of Randall and Rossini and of Lipsett, Johnson and Maass, were employed in a recalculation of activity coefficients. In spite of important differences between the above and the original values of $\overline{L}_1$ the results of the new calculations differ so little from the original ones that we refrain from giving them.

It seems probable however that work now being performed at other temperatures will introduce more important corrections. Some preliminary measurements[17] indicate that the variation of $\phi H - \phi H^\circ$ between 25 and 0° is much larger than is indicated by heat capacity data at 25°.

Summary

Data applicable to the calculation of the relative heat contents of the constituents of aqueous sodium chloride solutions have been assembled. They have been critically examined by a method convenient for their inter-comparison and for differentiation. The collected information has been supplemented by new measurements.

From all of the available data, the relative partial molal heat contents have been calculated for 25°. Activity coefficients calculated with the aid of these values are not very different from those originally calculated by Lewis and Randall.

[16] Ref. 14, p. 351.

[17] J. F. Chittum, Dissertation, University of Chicago.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WESTERN RESERVE UNIVERSITY]

THE SYSTEM CALCIUM CHLORIDE–MAGNESIUM CHLORIDE–WATER[1] AT 0, −15 AND −30°

BY C. F. PRUTTON AND O. F. TOWER

RECEIVED FEBRUARY 3, 1932 PUBLISHED AUGUST 5, 1932

Introduction

Sodium, calcium and magnesium chlorides occur together in sea water, most salt brines and salt deposits, and provide a commercial source of the above chlorides. In connection with the separation of these chlorides, data on the quaternary system calcium chloride–magnesium chloride–sodium chloride–water are of importance.

[1] Presented by C. F. Prutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Western Reserve University, 1928.

This work is a study in the ternary system calcium chloride–magnesium chloride–water, undertaken as a preliminary study to the quaternary system. The only data available on this ternary system is that of Lee and Egerton,[2] who give the 25° isotherm, and Smith and Prutton[3] who verified the existence of tachydrite—$CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$—and also found a second double salt at higher temperatures—$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$. The data of Van't Hoff, Kenrick and Dawson[4] were obtained in solutions saturated with sodium chloride. The occurrence of this second double salt suggested the possibility of still other double salts at temperatures below those investigated. The exact freezing points of solutions of calcium and magnesium chlorides are of interest in refrigeration where some use is made of the mixed chlorides for refrigerating brines.

Experimental

A. Materials Used.—Pure calcium chloride was obtained by dissolving C. P. calcium carbonate in C. P. hydrochloric (1 to 1) acid and precipitation of any magnesium present by boiling this solution with an excess of calcium oxide made by ignition of part of the calcium carbonate. The filtered solution was neutralized, concentrated by evaporation, and then cooled to 20° for about one day. Large crystals of the hexahydrate of calcium chloride separated. This crystallization was repeated six times.

Magnesium chloride was prepared by the solution of distilled magnesium metal (American Magnesium Corporation) in (1 to 2) C. P. hydrochloric acid. The slight excess acidity in solution was neutralized with C. P. magnesium oxide. The solution was filtered, concentrated and cooled to obtain crystals of the hexahydrate of magnesium chloride. The crystals were recrystallized twice from distilled water.

Both chlorides met with all tests on these salts as specified by Murray[5] for chemically pure reagents.

B. Method.—Solubilities were determined by the usual saturation method; samples of the saturated solutions and of the residues were taken for analysis. The residue method of Schreinemakers[6] was used to identify the solid phase present. All isothermal invariant points were approached from both sides of the equilibrium, and it was found that eight hours' agitation, in all cases, was sufficient time for equilibrium to be reached.

The cryostat used was a modification of that of Sinozaki and Hara.[7] Liquid ammonia was used as the cooling agent for temperatures down

[2] Lee and Egerton, *J. Chem. Soc.*, **123**, 711 (1923).

[3] Smith and Prutton, U. S. Patent 1,627,068.

[4] Van't Hoff, Kenrick and Dawson, *Z. physik. Chem.*, **39**, 27 (1902).

[5] Murray, "Standards and Tests for Reagent and C. P. Chemicals," 1927.

[6] Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

[7] Sinozaki and Hara, *J. Soc. Chem. Ind. Japan*, **29**, 262 (1926); *Tech. Rpts. Tôhoku Imp. Univ.*, Vol. VI, 2, 121 (1926).

to $-30°$ and liquid air for the lower temperatures. The cryostat bath was a four-liter Pyrex thermos silvered vacuum flask, 15 cm. in diameter and about 25 cm. deep. This was filled with a 50% ethyl alcohol–water mixture.

Temperature control of the bath could be automatically maintained at $\pm 0.1°$ for about twelve hours. With this variation in bath temperature, the temperature inside the solubility tube was maintained within $\pm 0.03°$ of the desired temperature.

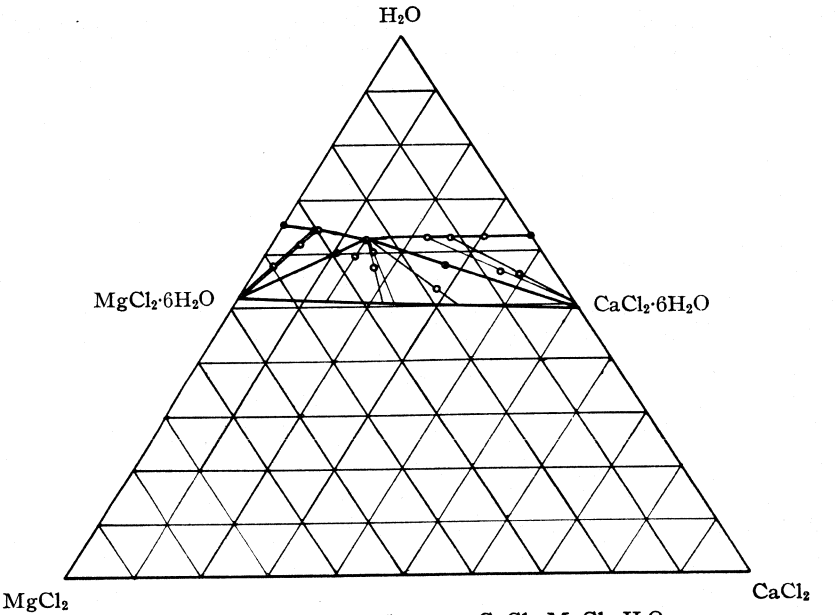


Fig. 1.—0° isotherms. System: $CaCl_2$–$MgCl_2$–H_2O.

The solubility tube was a large Pyrex test-tube (6 × 22 cm.) similar to that used by the Earl of Berkeley.[8] This tube was immersed in the cryostat bath to a depth of about 18 cm. and contained sufficient solution and crystals to fill the tube to a depth of about 7 cm.

Temperatures were measured by a multiple (six) junction copper-constantan thermocouple, inside the solubility tube, using a Leeds-Northrup portable potentiometer pyrometer. The uniformity of the wire used in the couple was checked and the couple calibrated in place; at the ice point, the freezing points of mercury and carbon tetrachloride, and the vaporizing temperature of solid carbon dioxide.

In the solutions and residues, calcium and total chloride were determined volumetrically, and the amounts of the two chlorides present cal-

[8] Earl of Berkeley, *Trans. Roy. Soc.* (*London*), **A203**, 189–215 (1904).

culated. The method of Blasdale[9] was used for precipitation of calcium oxalate and the precipitated calcium oxalate titrated by the well-known method using standard potassium permanganate. Mohr's method was used for the volumetric determination of total chlorides.

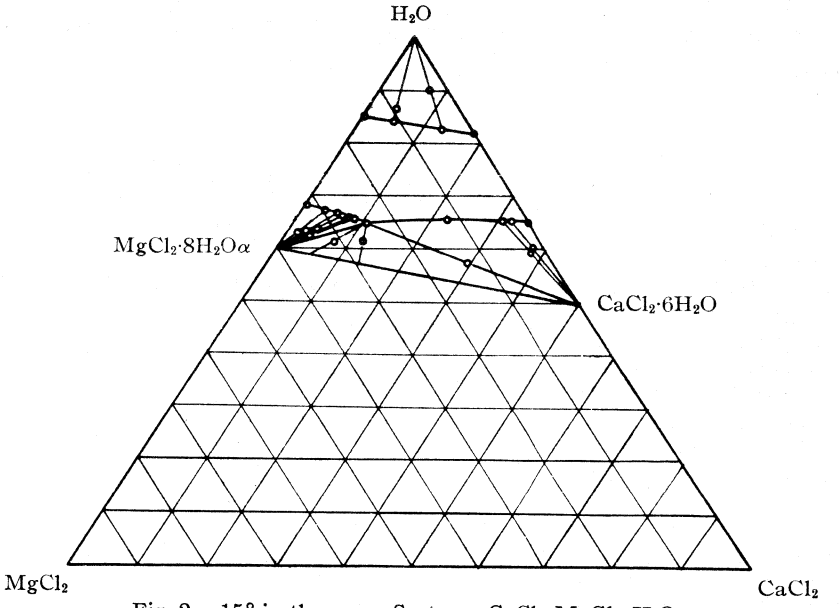


Fig. 2.—15° isotherms. System: $CaCl_2$–$MgCl_2$–H_2O.

The potassium permanganate solution used was standardized against Bureau of Standards sodium oxalate. The silver nitrate solution was

TABLE I

SOLUBILITY DATA AT 0°

Solid phase	Solution Grams/100 g. of solution $MgCl_2$	Solution Grams/100 g. of solution $CaCl_2$	Residue Grams/100 g. of residue $MgCl_2$	Residue Grams/100 g. of residue $CaCl_2$
$CaCl_2 \cdot 6H_2O$	0	37.32		
$CaCl_2 \cdot 6H_2O$	6.82	30.22		
$CaCl_2 \cdot 6H_2O$	11.95	25.10	5.01	37.42
$CaCl_2 \cdot 6H_2O$	14.94	22.12	7.60	36.02
$CaCl_2 \cdot 6H_2O$	22.83	14.89	14.96	27.47
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.86	13.82	27.54	13.69
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.78	13.90	26.17	15.44
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.81	13.81	19.15	28.47
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.70	13.78		
$MgCl_2 \cdot 6H_2O$	23.91	13.87	29.34	10.62
$MgCl_2 \cdot 6H_2O$	29.91	5.84	33.59	4.52
$MgCl_2 \cdot 6H_2O$	30.04	5.70	39.64	2.60
$MgCl_2 \cdot 6H_2O$	34.61	0.00		

[9] Blasdale, THIS JOURNAL, **31**, 918 (1909).

standardized using C. P. dry sodium chloride and also checked against standard ammonium thiocyanate solution which was compared with pure silver. Isothermal solubility curves at 0, −15 and −30° were determined. These solubilities are given in Tables I, II and III and shown graphically in Figs. 1, 2 and 3.

Figure 2a shows metastable solubility curves for calcium chloride hexahydrate and magnesium chloride hexahydrate at −15°.

TABLE II

SOLUBILITY DATA AT −15°

Solid phase	Solution Grams/100 g. of solution $MgCl_2$	Solution Grams/100 g. of solution $CaCl_2$	Residue Grams/100 g. of residue $MgCl_2$	Residue Grams/100 g. of residue $CaCl_2$
$CaCl_2 \cdot 6H_2O$	0	34.78		
$CaCl_2 \cdot 6H_2O$	0	34.77		
$CaCl_2 \cdot 6H_2O$	2.83	31.92	1.73	37.54
$CaCl_2 \cdot 6H_2O$	3.05	31.63		
$CaCl_2 \cdot 6H_2O$	3.90	30.50	2.56	37.81
$CaCl_2 \cdot 6H_2O$	11.97	22.42		
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 8H_2O\alpha$	24.21	10.78	30.47	7.95
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 8H_2O\alpha$	24.07	10.68	26.86	11.68
$CaCl_2 \cdot 6H_2O$ (metastable)	25.71	9.43	12.37	30.40
$CaCl_2 \cdot 6H_2O$ (metastable)	26.58	8.58	24.49	11.97
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ (metastable)	28.06	7.64	16.85	25.64
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ (metastable)	28.11	7.41	32.75	11.81
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ (metastable)	28.05	7.50	29.55	13.64
$MgCl_2 \cdot 6H_2O$ (metastable)	29.98	5.11	33.87	3.95
$MgCl_2 \cdot 6H_2O$ (metastable)	29.53	5.78		
$MgCl_2 \cdot 6H_2O$ (metastable)	33.86	0.00		
$MgCl_2 \cdot 8H_2O\alpha$	25.68	8.67	32.84	4.35
$MgCl_2 \cdot 8H_2O\alpha$	26.15	7.70	34.01	3.31
$MgCl_2 \cdot 8H_2O\alpha$	27.17	6.46	32.04	4.04
$MgCl_2 \cdot 8H_2O\alpha$	28.70	4.42	35.68	1.66
$MgCl_2 \cdot 8H_2O\alpha$	31.85	0.00		
Ice	0	12.23		
Ice	14.69	0		
Ice	10.85	5.00	9.16	4.27
Ice	4.01	13.35	2.50	7.40

The octahydrate of magnesium chloride obtained as the solid phase in the above solubility determinations is evidently the stable alpha form of this salt reported by Van't Hoff and Meyerhoffer,[10] as the solubility of the octahydrate in water at −15° agrees closely with the value reported by these workers.

There was no evidence of the metastable beta form of magnesium chloride octahydrate as reported by Van't Hoff and Meyerhoffer.

Magnesium chloride hexahydrate will not change to the octahydrate at −15° even when agitated for twenty-four hours with the solution.

[10] Van't Hoff and Meyerhoffer, *Z. physik. Chem.*, **27**, 75 (1898).

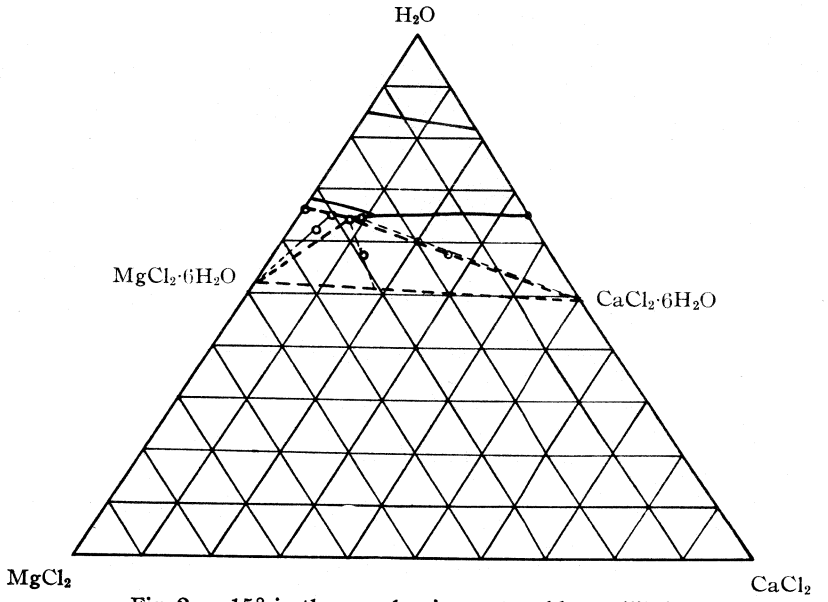


Fig. 2a.—15° isotherms, showing metastable equilibria.

This transition takes place rapidly when the solution is "seeded" with octahydrate crystals obtained by freezing a solution containing about 30% magnesium chloride at −30° or lower and then raising the temperature to −15°.

TABLE III

SOLUBILITY DATA AT −30°

Solid phase	Solution Grams/100 g. of solution $MgCl_2$	Solution Grams/100 g. of solution $CaCl_2$	Residue Grams/100 g. of residue $MgCl_2$	Residue Grams/100 g. of residue $CaCl_2$
$CaCl_2 \cdot 6H_2O$	0	32.92		
$CaCl_2 \cdot 6H_2O$	2.50	30.07	0.78	42.24
$CaCl_2 \cdot 6H_2O$	5.49	27.04	1.97	40.73
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 12H_2O$	8.51	23.76	10.85	26.50
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 12H_2O$	8.72	23.34	18.09	14.98
$CaCl_2 \cdot 6H_2O$ (metastable)	12.26	19.78	10.73	23.65
$CaCl_2 \cdot 6H_2O$ (metastable)	16.76	15.23		
$CaCl_2 \cdot 6H_2O$ (metastable)	25.55	7.40	15.16	24.77
$CaCl_2 \cdot 6H_2O$ (metastable)	27.20	6.14	18.59	20.01
$MgCl_2 \cdot 12H_2O$	22.19	0.00		
$MgCl_2 \cdot 12H_2O$	16.99	7.63	26.72	2.26
$MgCl_2 \cdot 12H_2O$	14.65	11.27	24.10	4.70
$MgCl_2 \cdot 12H_2O$	14.70	11.39	24.86	4.10
$MgCl_2 \cdot 12H_2O$	10.20	19.44		
$MgCl_2 \cdot 12H_2O$	9.94	19.81	21.12	9.05
Ice	20.47	0		
Ice	16.45	4.83	13.72	3.96
Ice	17.16	6.18	5.34	13.57
Ice	0.00	25.03		

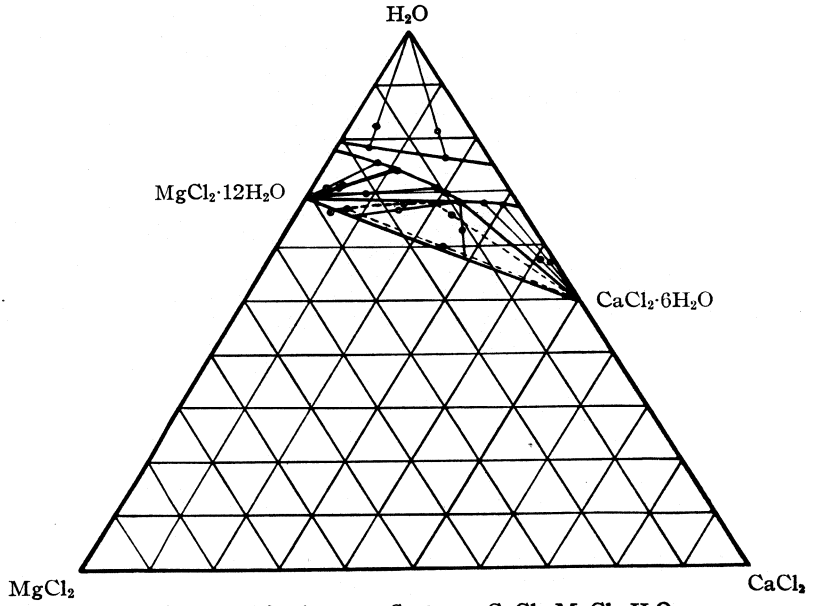


Fig. 3.—30 isotherms. System: $CaCl_2$–$MgCl_2$–H_2O.

Determination of Monovariant Points.—The following monovariant points were determined. Temperatures were determined by the thermometric method and compositions by the saturation method.

Phases in equilibrium	Temperature, °C.	Composition
1. $MgCl_2 \cdot 6H_2O$		26.40 $MgCl_2$
$MgCl_2 \cdot 8H_2O\alpha$	− 6.7	9.90 $CaCl_2$
$CaCl_2 \cdot 6H_2O$		
Satd. soln.		
2. $MgCl_2 \cdot 12H_2O$		23.23 $MgCl_2$
$MgCl_2 \cdot 8H_2O\alpha$	−20.7	10.56 $CaCl_2$
$CaCl_2 \cdot 6H_2O$		
Satd. soln.		
3. $CaCl_2 \cdot 6H_2O$		2.93 $MgCl_2$
$MgCl_2 \cdot 12H_2O$	−52.2	27.40 $CaCl_2$
Ice		
Satd. soln.		

Figure 4 shows the completed ternary diagram plotted on triangular coördinates.

The curves for temperatures above 0°, from data of Van't Hoff, are shown by broken lines, as these results were obtained in solutions saturated with sodium chloride.

Points B, C and F are the monovariant points at −6.7, −20.7 and −52.2°, respectively. Points A, D, E and point between B and C, are isothermal monovariant points at 0, −24.0, −30 and −15°, respectively.

The light lines with arrows in the various areas indicate the direction in which the composition of a solution changes, on progressive cooling, due to separation of crystals of the stable solid phase in the given area.

Arrows on heavy lines between phase areas indicate how the solution changes when two solids separate from solutions on cooling.

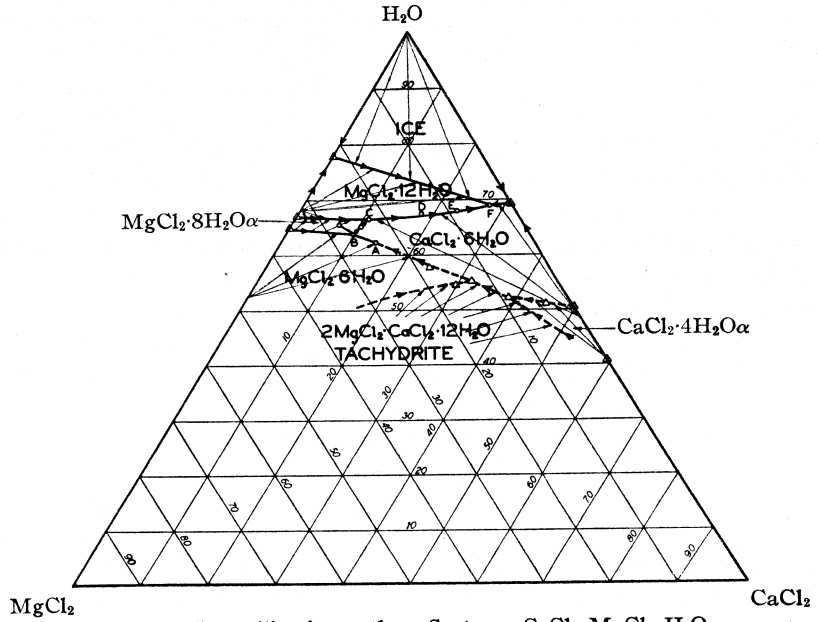


Fig. 4.—Crystallization paths. System: $CaCl_2$–$MgCl_2$–H_2O.

Summary

1. The solubility relations of the ternary system, calcium chloride–magnesium chloride–water, at 0, −15 and −30° have been determined.

2. There is no evidence of double salt formation in this system at the temperatures studied.

3. Temperatures and compositions of ternary monovariant points have been determined.

4. The existence of $MgCl_2 \cdot 8H_2O\beta$ reported by Van't Hoff and Meyerhoffer, was not detected.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IONIZATION OF ORGANIC ACIDS

BY HUGH M. SMALLWOOD

RECEIVED FEBRUARY 4, 1932 PUBLISHED AUGUST 5, 1932

The physical interpretation of the effects of substituent groups upon the acid strength of organic compounds has been the subject of much discussion. Ostwald[1] began the attack on the problem by classifying the various groups as positive or negative according to whether they caused a decrease or an increase in acidity. Since then numerous papers have dealt with the subject in a more quantitative manner, but the treatments have been empirical throughout, in that they have established relationships between the ionization constants of various acids without attempting any numerical correlation of the effect of a particular substituent with the properties of that substituent.

As a result of the recent activity in the measurement of dipole moments, it is natural to suppose that the extent of ionization of an organic acid is affected by the dipoles present in the molecule. This possibility has been considered qualitatively by Wolf,[2] and Langmuir,[3] and, in a more general way, by Briegleb.[4] The first named author suggested that the acid properties of the carboxyl group are due to the influence of the dipole associated with the carbon–carbonyl oxygen bond. Langmuir pointed out that the dipole associated with the carbon–chlorine bond in mono-chloroacetic acid should facilitate the ionization of the molecule. Briegleb concluded that it is not possible to give a quantitative treatment of the subject, due to the inability of calculating the various free energies of hydration, and of allowing for the effect of association. Although these difficulties would undoubtedly prevent the development of a complete theory, it is possible to give an approximate treatment of the effect of dipole moments upon ionization. Such a treatment may be obtained as follows.

The ionization constant of a weak acid is a measure of the free energy change in the reaction

$$HA_{aq} \longrightarrow H^+_{aq} + A^-_{aq} + \Delta F$$

For purposes of calculation it is simpler to carry out this process in the following manner

$$HA_{aq} \longrightarrow HA_g + \Delta F_1$$
$$HA_g \longrightarrow H^+_g + A^-_g + \Delta F_2$$
$$H^+_g \longrightarrow H^+_{aq} + \Delta F_3$$
$$A^-_g \longrightarrow A^-_{aq} + \Delta F_4$$

[1] W. Ostwald, *J. prakt. Chem.*, **31**, 300 (1885); *Z. physik. Chem.*, **3**, 170, 241, 369 (1889).

[2] K. L. Wolf, *ibid.*, **3B**, 128 (1929).

[3] I. Langmuir, *Chem. Rev.*, **6**, 465 (1929).

[4] G. Briegleb, *Z. physik. Chem.*, **10B**, 205 (1931).

Then

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 = -RT \ln K_a \quad (1)$$

where K_a is the ionization constant of the acid HA and the free energy changes are defined by the various reactions. Of these four free energy terms the second is important for the present purpose. It is, of course, equal to $\Delta E + p\Delta V - T\Delta S$, where the symbols have their usual significance. ΔE, the energy change accompanying the removal of a proton from the neutral HA molecule, is made up of four parts: first, the work of altering the electron distribution from that corresponding to the mainly non-polar binding, present in the neutral molecule, to a distribution corresponding to two ions, H^+ and A^-, situated at a distance equal to their equilibrium separation in the undistorted molecule; second, the work against the Coulomb attraction necessary to remove the H^+ to infinity; third, the change in the polarization energy of the anion due to the removal of H^+; and, finally, the work of removal of H^+ from the electric field due to any dipoles in the anion. Of these four contributions to the free energy of ionization, the last is the only one of immediate interest. In general, it is small in comparison with the other energy terms, but it may be brought into prominence, and the difficulties of calculating the other terms may be avoided by comparing the ionization constants of two acids differing mainly in the group moments present in their anions. Let the other member of such a pair be represented by HA'. The corresponding ΔF's will be designated by the same subscripts as have been used for HA, but with the addition of primes. Then, if the anions are sufficiently similar, it may be supposed that $\Delta F_2 - \Delta F_2'$ will equal the difference between the work of removal of H^+ from the dipole field of A^- and the work of removal from that of A'^-, say $\epsilon - \epsilon'$. Similarly, if the two compounds are not too different, it may be expected that $\Delta F_1 = \Delta F_1'$ and $\Delta F_4 = \Delta F_4'$. Of course $\Delta F_3 = \Delta F_3'$ for all acids. Since

$$\Delta F' = \Delta F_1' + \Delta F_2' + \Delta F_3' + \Delta F_4' = -RT \ln K_a' \quad (2)$$

one obtains by subtracting (2) from (1)

$$\Delta F - \Delta F' = \epsilon - \epsilon' = -RT \ln \frac{K_a}{K_a'} \quad (3)$$

The work of removal ϵ is $-e\Phi$, where e is the charge on the hydrogen ion, and Φ is the potential due to the group moments of the anion calculated at the point occupied by the hydrogen nucleus in the undissociated molecule. Similarly, $\epsilon' = -e\Phi'$. By substitution

$$\log \frac{K_a}{K_a'} = \frac{e(\Phi - \Phi')}{2.3kT} \quad (4)$$

The dielectric constant of water, the medium in which the dissociation actually takes place, does not appear in this equation because the energy terms affected by this quantity occur in the free energies of hydration, which have been assumed to cancel. This is not true of some analogous calculations by Bjerrum,[5] in which the dielectric

[5] N. Bjerrum, *Z. Physik. Chem.*, **106**, 219 (1923).

constant of water does appear. The latter calculations evaluate the ratio of the first and second ionization constants of some dibasic acids, taking account of the energy necessary to remove the second hydrogen ion from the field of the negative charge left by the first ionization, the whole process being assumed to take place in the solvent. This discrepancy between Bjerrum's work and the present treatment is only apparent, since in his case a cyclic process could not lead to cancellation of the free energies of hydration, due to the difference in charge of the two anions compared (HA^- and $A^=$). The inclusion of this change in the free energies of hydration involves the introduction of the dielectric constant of water.

It might also be pointed out that the present treatment avoids the difficulty of allowing for the association of the neutral acid molecules in solution, by means of the assumption that the extent of the association of the unsubstituted acid is practically the same as that of the substituted.

Equation (4) will first be applied to the rather extreme case of formic acid and methyl alcohol. It is necessary to assume detailed models of the molecules under discussion: that used for formic acid is shown in Fig. 1, together with the necessary dimensions. The potential at the hydrogen nucleus is made up of one contribution from the C=O group moment and one from the CH group moment, the potential of a dipole of strength μ being given by the relation

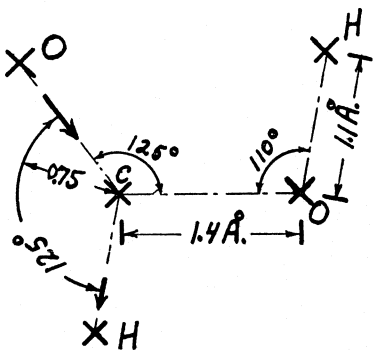


Fig. 1.—Model of formic acid.

$$\Phi = \frac{\mu}{r^2} \cos \angle (\mu, r) \qquad (5)$$

where r is the radius vector from the dipole to the point at which the potential is calculated. The C—O group moment is neglected, since it is present with the same orientation in both molecules. Φ', the analogous quantity for methyl alcohol, is due to three CH moments. Here, however, it may be supposed that the methyl group can rotate about the C—O bond. Formic acid is presumably a plane molecule, since the strong interaction between the OH and CO moments completely prevents rotation at ordinary temperatures.[6] To take into account the rotation of the methyl group it is necessary to average Φ' over the azimuthal angle about the CO bond.

This averaging is effected as follows: a set of coördinates is so chosen that (1) the X-axis coincides with the axis of rotation in the molecule, and (2) the group moment, whose potential is to be averaged, is contained in the XY plane. Then

$$\bar{\Phi} = \frac{1}{\pi}\int_0^\pi \Phi d\varphi \qquad (6)$$

$$= \frac{A}{\pi}\int_0^\pi \frac{d\varphi}{(p^2 - q^2\cos\varphi)^{3/2}} + \frac{B}{\pi}\int_0^\pi \frac{\cos\varphi d\varphi}{(p^2 - q^2\cos\varphi)^{3/2}}$$

[6] L. Meyer, *Z. physik. Chem.*, **8B**, 27 (1930).

where φ is the azimuth about the axis of rotation, and

$$\left.\begin{aligned} A &= \xi(x_H - x_m) - \eta y_m;\ B = \eta y_H \\ p^2 &= (x_H - x_m)^2 + y_H^2 + y_m^2;\ q^2 = 2\, y_H y_m \end{aligned}\right\} \quad (7)$$

In equation (7) ξ and η are, respectively, the x and y components of the group moment; x_H, y_H the coördinates of the ionizing hydrogen nucleus; and x_m, y_m those of the group moment. Evaluation of the integrals[7] leads to the expression

$$\bar{\Phi} = \frac{2}{(p^2 + q^2)^{1/2}\pi}\left\{\frac{1}{p^2 - q^2}\left[A + \frac{Bp^2}{q^2}\right]E - \frac{BK}{q^2}\right\} \quad (8)$$

where K and E are, respectively, the complete elliptic integrals of the first and second kinds for the modulus

$$k = \left(\frac{2\,q^2}{p^2 + q^2}\right)^{1/2} \quad (9)$$

The values of the group moments used for these calculations, together with the necessary molecular dimensions, have been summarized in Table I. In addition to these, the following values have been used. The angle between the oxygen valence bonds has been assumed to equal 110°, the aliphatic carbon bonds to possess tetrahedral symmetry, the benzene nucleus to be a regular plane hexagon. Group moments have been assumed to lie along the valence bonds and to be situated at a point 0.75 Å. from the carbon nucleus (0.6 Å. from the oxygen nucleus in OH). A moment whose positive end is farthest from the carbon nucleus (from the oxygen nucleus in OH) is written + and *vice versa*. The magnitudes of the group moments have been obtained from the resultant moment of the corresponding mono-benzene derivative, as listed by Smyth,[8] with the assumption that $\mu_{CH} = +0.5$. Reasons for the use of these values will be presented in a future article. The group moments of the nitro and cyano groups have been located 0.4 Å. beyond the N and 0.75 Å. beyond the C nuclei, respectively.

TABLE I

Group	Internuclear distance, Ångström units	Electric moment × 10^{18}	Group	Internuclear distance, Ångström units	Electric moment × 10^{18}
CH	...	+0.5	CCN	d_{CC}=1.5	−3.4
C—O	1.4	...	C—NO_2	d_{CN}=1.44	−3.4
C=O	...	−2.2	C—$C_{aliph.}$	1.5	0
CF	...	−0.95	C≡C	1.2	0
CCl	...	−1.05	C—$C_{arom.}$	1.4	0
CBr	...	−1.0	OH	1.1	+1.6
CI	...	−0.8			

Application of equations (4) and (8) to formic acid and methyl alcohol leads to a calculated value of the ionization constant of the latter compound of the order of magnitude 10^{-17}. This quantity has not been measured, but it is safe to assume that this calculated value is too high, since smaller ionization constants have been measured. The discrepancy is due to the neglect of the resonance energy of the carboxyl ion, recently pointed out by

[7] *Cf.* Bierens de Haan, "Nouvelles Tables d'Intégrales Définies," Leiden, 1867, Table 67, p. 102, equation (3) and (4). Equation 4, as given by de Haan, is incorrect. The correct value for this integral has been used in the present calculations.

[8] C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, pp. 195 and 203.

Pauling.[9] According to his estimations, this effect should increase the strength of formic acid to about 10^{13} times that of methyl alcohol. Taking into account both the dipole repulsion and the resonance energy, the expected value for the ionization constant of methyl alcohol is $\sim 10^{-30}$, an entirely reasonable figure. It may be concluded that the acid properties of the carboxyl group are due in part to the substitution of a repelling carbonyl group moment for two attracting CH dipoles, and in part to the resonance energy of the carboxyl ion, the two effects being of approximately the same importance.

A more satisfactory test of the present treatment may be obtained from a study of the substituted acetic, propionic and benzoic acids and the substituted phenols. The calculations are entirely analogous to the previous case, and need not be given in detail. It has seemed best to compare the calculated change in energy of ionization, $(\Delta E - \Delta E')_{\text{calcd.}} = -e(\Phi - \Phi')$, with the experimental values, $(\Delta E - \Delta E')_{\text{obs.}} = 2.3RT \log K_a/K_a'$. These quantities, expressed in kilocalories per mole, are listed in Table II for most of the substituted acids for which data are available and which are amenable to treatment. The list is greatly diminished by the fact that the present method of calculation is limited to molecules in which there is only one effective possibility of rotation between the substituent group moments and the ionizing hydrogen. Further limitations will be mentioned below. Inspection of Table II shows that there is good agreement in some cases and definite disagreement in others. The causes of these discrepancies are, in most cases, apparent.

The first of such departures is found for the poly substituted acetic acids. These deviations must be ascribed to alterations of the magnitudes and directions of the group moments due to the intense interaction of the substituents. The data necessary to show that this is the case are available, if it be assumed that the effects of distortion and induction in di- and trichloroacetic acids are the same as in methylene chloride and in chloroform, respectively. Using the valence angles deduced from the x-ray measurements of Bewilogua[10] and group moments calculated from the molecular moments listed by Smyth,[11] together with the assumption that the CH moment equals 0.5×10^{-18}, one obtains the figures listed in the last column of Table II. These are seen to be in good agreement with the experimental values.

Further discrepancies are apparent in the compounds containing nitro groups. These are most probably caused by the use of a single resultant moment for this substituent. Taking the complexity of the nitro group into account would improve the agreement but, in the absence of data

[9] L. Pauling, *Proc. Natl. Acad. Sci.*, **18**, 293 (1932), and personal communications.

[10] L. Bewilogua, *Physik. Z.*, **32**, 265 (1931).

[11] Ref. 8, pp. 192 and 201.

TABLE II

HA	HA′	$\Delta E - \Delta E'$ obs.[a]	$\Delta E - \Delta E'$ calcd.	(k cal./mole calcd.
CH_2FCOOH		2.8	3.5	
$CH_2ClCOOH$		2.6	3.7	
$CH_2BrCOOH$		2.6	3.6	
CH_2ICOOH		2.3	3.1	
$CH_2CNCOOH$	CH_3COOH	3.1	9.2	
CHF_2COOH		4.8	6.9	
$CHCl_2COOH$		4.7	7.5	6.2[b]
CCl_3COOH		6.6	11.2	8.7[b]
$CH_3C{\equiv}CCOOH$		2.9	2.7	
$CH_3CHClCOOH$	C_2H_5COOH	2.8	3.7	
o-C_6H_4ClOH		1.2	1.3	
p-C_6H_4ClOH		0.8	3.5	
o-$C_6H_4NO_2OH$	C_6H_5OH	3.9	11.0	
m-$C_6H_4NO_2OH$		2.7	7.4	
p-$C_6H_4NO_2OH$		3.8	6.6	
m-C_6H_4FCOOH		0.4	1.9	
o-$C_6H_4ClCOOH$		1.8	−0.4	0.7[c]
m-$C_6H_4ClCOOH$		0.5	2.1	
p-$C_6H_4ClCOOH$		0.2	2.3	
o-$C_6H_4BrCOOH$		1.8	−0.6	0.6[c]
m-$C_6H_4BrCOOH$		0.4	2.1	
p-$C_6H_4BrCOOH$	C_6H_5COOH	(0)	2.1	
o-C_6H_4ICOOH		1.8	−0.3	0.5[c]
m-C_6H_4ICOOH		0.5	1.8	
o-$C_6H_4NO_2COOH$		2.7	2.3	
m-$C_6H_4NO_2COOH$		1.0	4.6	
p-$C_6H_4NO_2COOH$		1.1	4.7	

[a] Calculated from ionization constants at 25° listed by H. Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, 1914.

[b] Corrected for interaction of group moments.

[c] Calculated assuming rotation to be completely frozen out.

indicating the magnitudes of the N=O and C—N moments, it has not seemed worth while to attempt a more detailed calculation for these compounds. The agreement shown by *o*-$C_6H_4NO_2COOH$ is probably fortuitous, the effect of hindered rotation (discussed below) counterbalancing the effect of using a resultant moment for the nitro group.

The most serious discrepancy is shown by the ortho halobenzoic acids, for which compounds the calculations indicate that the substituent halogen should cause a decrease in acid strength. This is undoubtedly due to a hindered rotation of the carboxyl group. If it be assumed that the rotation is entirely frozen, the ionizing hydrogen being as far from the substituent as possible, the figures listed in the last column of Table II are obtained.

Finally, it should be pointed out that there is a pronounced tendency for the calculated values to be higher than the observed. In all probability

this is due to the neglect of the change in polarization energy of the anion upon substitution (the third part of ΔE, p. 3049). This cannot be allowed for numerically, since the electric intensities are so great that polarizabilities calculated from refractive indices no longer have any meaning. It is, however, worth noting that this divergence is roughly proportional to the polarizabilities of the substituent groups.

The only definite discrepancy that has not been accounted for is shown by cyanoacetic acid. Judging from the other results, this departure is too large to be explained by the omission of the polarization energy of the anion. The experimental value for *p*-bromobenzoic acid is enclosed in parentheses because it is of a lower order of accuracy than the other figures.

It has been shown empirically by a number of authors, in particular by Derick,[12] that the change in free energy of ionization upon substitution is an additive property of the nature and relative position of the substituent. This rule is explained by the present treatment as follows. According to the assumptions used above, the change in free energy equals the change in energy of removal of the hydrogen ion. The latter quantity is proportional to the electrostatic potential of the group moment of the substituent, and since the potential is an additive quantity the change in the free energy of ionization must also be additive. As an illustration of this rule, it might be mentioned that $\Delta E - \Delta E'$ for picric acid (compared with phenol) is equal to the energy difference for *p*-$C_6H_4NO_2OH$ plus twice that for *o*-$C_6H_4NO_2OH$.

Numerous papers have dealt with the effect of removing the substituent along the straight chain of an aliphatic acid. According to equation (5) the effect of the substituent should vary with the inverse square of the distance, provided the angle between the group moment and the radius vector to the ionizing hydrogen remains the same. In general, this will not be the case, and it is this angle which is most important in determining the magnitude of the effect. The large number of rotations, which take place to a more or less limited extent in a straight chain, precludes applying the present calculations to any aliphatic acids except those substituted in the alpha position.

Finally, it is desirable to consider briefly the assumptions underlying equations (4) and (8). First, the cancellation of the free energies of hydration, to within 1–2 k. cal., seems probable upon recalling that these quantities are dependent in part upon the orientation of the water dipoles in the field of the negative charge, if any, and in the field due to the dipoles of the particle; and in part to dispersion attraction. The first effect cannot be altered greatly by substitution since the domain of the —COO^- group is not affected. The increase in diameter of the anion occurs in a region relatively

[12] Derick, THIS JOURNAL, **33**, 1167 (1911); **34**, 74 (1912); Derick and Kamm, *ibid.*, **39**, 38 (1917); Derick and Hess, *ibid.*, **40**, 537 (1918).

far from the location of the charge and therefore in a region where this effect is least.[13] The orientation in the dipole field and the dispersion attraction probably differ for the substituted and unsubstituted acids. They should, however, affect by the same amount the free energy of hydration of the anion and that of the undissociated molecule so that they cancel upon adding ΔF_1 to ΔF_4.

It is necessary to consider in more detail the assumptions made concerning the extent of rotation about valence bonds. It has been assumed that there is no rotation in the carboxyl group, or in the ortho halobenzoic acids, but that in all the other compounds treated the acid group rotates freely with respect to the rest of the molecule. These suppositions may be justified qualitatively as follows. Whether or not rotation takes place depends on the accompanying change in the internal energy of the molecule. This energy is made up of (1) dipole attractions or repulsions, (2) changes in polarization, due to changes in dipole fields, (3) steric repulsions.[14] Only the first of these terms can be calculated, at present; even here the accuracy is probably not very great due to the close approach of the group moments. The direction and extent of the other two terms may at least be estimated, the first from the polarizabilities of the groups between the rotating dipoles, and the second from internuclear distances. Upon applying the calculation of the dipole energy to the carboxyl group, it is found that this term is very large. Since steric hindrance and polarization should be negligible for this group, it is almost certain that rotation is frozen out, as was indicated by Meyer.[6] In the mono-halo-acetic acids the dipole energy is again large, but here one would expect appreciable change in the polarization energy. The dipole term favors that position of the molecule in which the ionizing hydrogen is as near as possible to the substituent. The polarization energy has the opposite effect. In the configuration corresponding to minimum dipole energy there must be considerable steric hindrance. The net effect cannot be predicted with any certainty, but it seems most probable that rotation is nearly free. In any case the assumption of free rotation is not critical for these compounds, since here Φ does not change greatly upon rotation.

This is not true, however, of the ortho phenols and the ortho benzoic acids, where Φ changes sign as φ goes from 0 to π. In both of these classes of compounds there is a relatively small dipole energy tending to hold the ionizing hydrogen near to the substituent. No steric hindrance is to be expected in o-C_6H_4ClOH, but the polarization energy, due to the easily deformable aromatic C–C bonds, should be enough to counteract the dipole energy, so that rotation about the C–O bond may be expected to take place.

[13] T. J. Webb, THIS JOURNAL, **48**, 2589 (1926).

[14] The change in dispersion energy is negligible for the compounds under consideration. *Cf.* H. A. Stuart, *Phys. Rev.*, **38**, 1372 (1931).

The ortho halobenzoic acids differ from the phenols in that the position of minimum dipole energy for the former compounds involves so great a steric hindrance that the configuration becomes extremely improbable. Rather than attempt a discussion based on partially restricted rotation, it has seemed best to include values based on the extreme assumption of no rotation, but with the ionizing hydrogen fixed at the farthest point from the substituent. Interactions between the substituent and the acid group in the meta and para compounds are too slight to affect the rotation.

Extremely interesting information on the gradual loosening of a restricted rotation might be obtained by comparing the ionizations of ortho substituted benzoic acids with that of benzoic acid over as wide a temperature range as possible. Similar studies on phenols might also be of value in this connection, but here it would probably be necessary to go to lower temperatures. From the present discussion it is to be expected that at sufficiently low temperatures the ionization of *o*-C_6H_4ClOH will approach that of phenol, and that at high enough temperatures that of *o*-C_6H_4Cl-COOH will approach that of benzoic acid. It is not possible to calculate the temperatures at which these changes should take place; it may be that they are beyond the experimental range. By choosing the substituent groups suitably, however, it should be possible to find compounds in which the free energies of ionization, relative to the unsubstituted acid, change profoundly with the temperature.

Indications of the expected change are definitely shown by the few compounds for which Scudder gives data at more than one temperature. These data are listed in Table III, the $(\Delta E')$'s being obtained from the ionization constants of benzoic acid at the appropriate temperatures. It is apparent that the strengthening effect of the substituent in the ortho compounds decreases with increasing temperature, while the effect of the substituent in the meta position is essentially independent of the temperature. This is in entire accord with the predictions of the present treatment: in the ortho compounds there is sufficient steric hindrance to hold the ionizing hydrogen in a region where the substituent's group moment repels the H^+ and so causes an increase in acidity. As the temperature increases the amplitude of oscillation about the bond between the COOH and C_6H_4X groups increases, with the result that the H^+ spends more and more time in regions of decreased repulsion or even of attraction. At sufficiently high temperatures it is to be expected that *o*-$C_6H_4ClCOOH$ will be weaker than benzoic acid. No such effect is found or expected in the meta acids since in these compounds the steric effects, if any, should be essentially the same as in the unsubstituted acid. The five compounds listed in Table III are by no means enough to establish the present interpretation, but it may be considered that they bring to it definite confirmatory evidence.

TABLE III

$(\Delta E - \Delta E')_{obs.}$ K. cal./Mole.

t, °C.	0°	25°	50°	90°
o-$C_6H_4ClCOOH$	...	1.8	1.6	1.4
o-C_6H_4ICOOH	...	1.8	1.6	1.4
o-$C_6H_4NO_2COOH$	3.0	2.7	2.5	2.2
m-C_6H_4ICOOH	...	0.5	...	0.4
m-$C_6H_4NO_2COOH$	0.9	1.0	1.0	1.1

Two further inferences may be drawn from this treatment of acidity. In the first place, it has not been necessary to take into account any transmission of the dipole forces through the electronic structure between the ionizing hydrogen and the polar substituent. This amounts to neglect of the alteration of the induced moments in this region. That the permanent moments predominate is to be expected, since they are, as a general rule, considerably larger than the induced moments. Second, the strengthening effect of unsaturation is due, not to a specific property of the double or triple bond, but to the removal of CH dipoles which, in the saturated acid, are so oriented as to attract the hydrogen ion and thus hinder ionization.

From the foregoing discussion it may be concluded that the change in ionization of an organic acid caused by substitution may be accounted for numerically, at least in the absence of disturbing effects, by assuming as its cause the change in electrostatic repulsion or attraction between the hydrogen ion and the dipoles of the anion of the acid.

In conclusion it is a pleasure to express my indebtedness to Professor K. F. Herzfeld and to Professor J. B. Conant for valuable suggestions in the preparation of this manuscript.

Summary

It has been shown that the changes in ionization of organic acids upon substitution of polar groups are, to a large extent, determined by the magnitude and orientation of the electric moments associated with the substituent groups.

CAMBRIDGE, MASSACHUSETTS

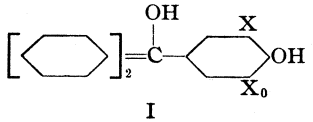
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS. III[1]

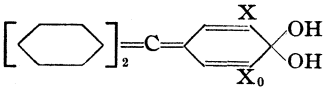
BY LEIGH C. ANDERSON AND M. B. GEIGER[1]

RECEIVED FEBRUARY 8, 1932 PUBLISHED AUGUST 5, 1932

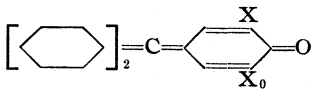
Previous papers from this Laboratory[2] have shown that a marked change in absorption spectra occurs on changing from the colorless benzenoid *p*-hydroxytriphenylcarbinols to the corresponding colored carbinols. These spectroscopic data were interpreted as constituting further evidence for the existence of a quinonoid tautomer (II) of the corresponding benzenoid carbinol (I). The fact that the colorless carbinol possesses a benzenoid structure has not been doubted, and the structure of the corresponding fuchsone (III) has never been called in question. Explanations for the



I



II



III

existence of the colored carbinol, however, have implied the suggestion that it is a hydrate of the fuchsone,[3] or that it is a mixture of the benzenoid carbinol with small amounts of the highly colored fuchsone as impurity. Chemical evidence by Gomberg and co-workers[4] has definitely shown that the colored carbinol is not an impure benzenoid carbinol.

This work was undertaken in order to obtain further data concerning this class of compounds with the hope that certain effects that were observed in previous work in regard to the position and height of the absorption bands might now be explained.

[1] The material in this and the succeeding paper comprises a portion of a thesis presented by M. B. Geiger to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

[2] (a) Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928); (b) Anderson, *ibid.*, **51**, 1889 (1929).

[3] (a) Auwers and Schröter, *Ber.*, **36**, 3247 (1903); (b) Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, **49**, 1546 (1927). In the latter article the statement is made that "Gomberg has shown that fuchsone readily takes up water to form the quinoid hydrate." The word hydrate in this connection is ambiguous and was not used by Gomberg. He states in the article from which the above inference was drawn [THIS JOURNAL, **35**, 1037 (1913)] "nor does either of the two molecules contain water of crystallization."

[4] Gomberg, THIS JOURNAL, **35**, 1035 (1913); Gomberg and Van Stone, *ibid.*, **38**, 1577 (1916).

In Figs. 1, 2, 3 and 4, respectively, are given the curves for the quantitative spectra of the methane, colorless carbinol (except for the 3-chloro-), colored carbinol, and the fuchsone of each of the following: 3-chloro-4-hydroxy-, 3-bromo-4-hydroxy-, 3,5-dichloro-4-hydroxy- and 3,5-dibromo-4-hydroxytriphenylcarbinol. The methanes and colorless carbinols are undoubtedly benzenoid in constitution while the fuchsones contain a quinonoid nucleus.

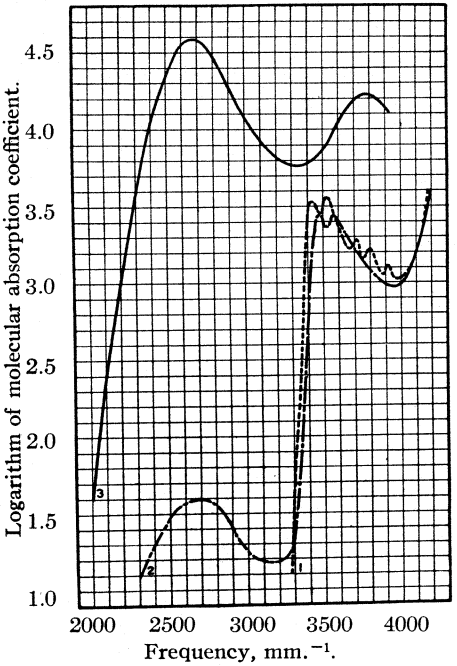


Fig. 1.—3-Chloro-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchsone.

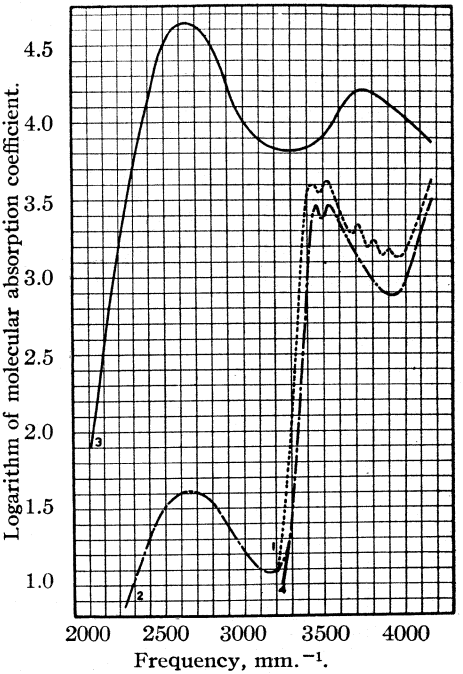


Fig. 2.—3-Bromo-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchsone; 4, carbinol, colorless.

The similarity of the curves for the corresponding derivatives in each of the groups is very striking. All of the fuchsones have an intense absorption band on the edge of the visible region of the spectrum and another band in the ultraviolet. The methanes have no absorption in the visible region but have a series of bands in the ultraviolet between frequencies 3400 and 4000 mm.$^{-1}$. The benzenoid carbinols show no absorption in the visible region of the spectrum, and their ultraviolet absorption consists of a number of fine bands very similar to those of the methanes. The colored carbinols have spectra resembling both the fuchsones and the benzenoid carbinols in that they have an absorption band in the visible region of the spectrum and the ultraviolet absorption is practically identical with the ultraviolet absorption of the colorless carbinol.

The progressive substitution of one chlorine atom, one bromine atom, two chlorine atoms and two bromine atoms for the hydrogens in the ortho positions to the nuclear hydroxyl group in the 4-hydroxytriphenylcarbinol compounds causes a shift in the intense absorption band for the fuchsones toward the longer wave lengths. A similar change is noted for the band in the visible for the colored carbinols and for the two most persistent bands in the ultraviolet for the methanes, colorless carbinols and colored carbinols.

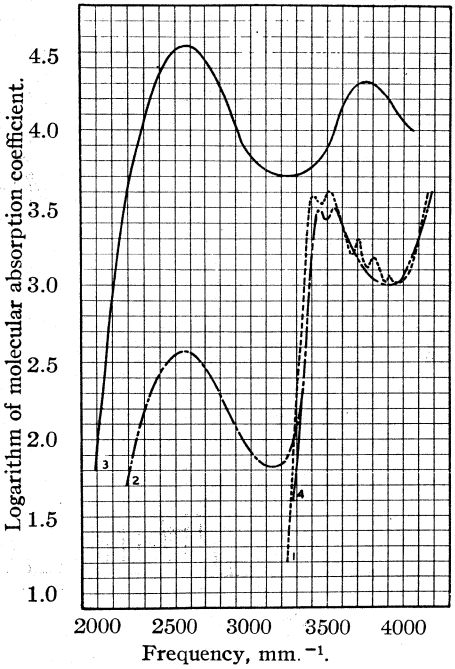


Fig. 3.—3,5-dichloro-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchsone; 4, carbinol, colorless.

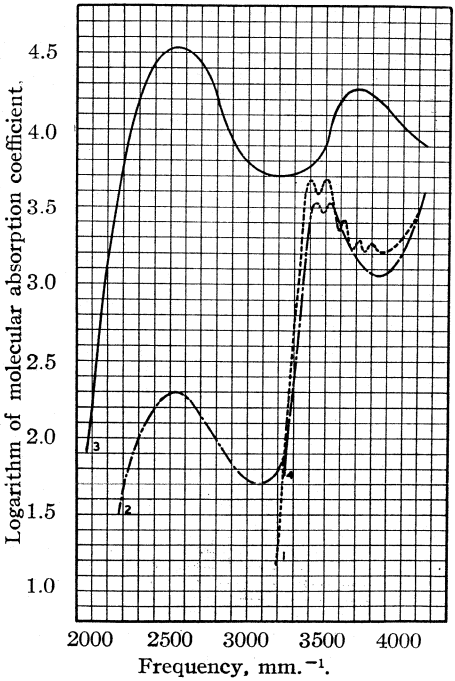


Fig. 4.—3,5-Dibromo-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchsone; 4, carbinol, colorless.

The height of the quinonoid band[5] for the various fuchsones is approximately the same. In all cases which have been observed the quinonoid band for the colored carbinols is much lower than the quinonoid band for the fuchsones; Table I lists the heights of the quinonoid bands of the fuchsones and the colored carbinols expressed as logarithms of the molecular absorption coefficients. If the colored carbinol were a hydrate of the corresponding fuchsone such a variation would not be expected. The curve for the hydrate calculated on the basis of fuchsone should be 93.5%

[5] The band which occurs in the edge of the visible and near ultraviolet in the spectra of these fuchsones and colored carbinols will be called, for convenience of description, the quinonoid band.

TABLE I

HEIGHTS OF THE QUINONOID BANDS

3-X,5-X$_0$,4-hydroxy-triphenylcarbinol	a X H	a X$_0$ H	b X H	b X$_0$ Cl	c X H	c X$_0$ Br	d X Cl	d X$_0$ Cl	e X Br	e X$_0$ Br
Fuchsones	4.48		4.58		4.64		4.54		4.53	
Colored carbinols	2.52		1.59		1.61		2.57		2.30	

as high as the curve for the fuchsone. The difference which has been found in the height of the bands is, therefore, much more than would be accounted for by the effect of a molecule of water in so heavy a molecule as the fuchsone, even assuming that it were a hydrate and that it would all remain hydrated in so dilute an ether solution.

It has been found that the colored carbinols with symmetrical substitution in the nucleus (a, d, e, Table I) have quinonoid bands whose heights are of the same order of magnitude. The height of the quinonoid bands for the colored carbinols with unsymmetrical substitution (b and c, Table I) is even lower than the band for those with symmetrical substitution, but when compared with each other, they are of the same order of magnitude.

Figure 5 gives the position of the peaks or frequencies of maximum absorption of the bands for the colored carbinols (Q) and the fuchsones (F) of the different carbinols studied in this investigation and also includes those described in the papers previously referred to. It will be noted that in the case of some of the carbinols the frequency of maximum absorption of the quinonoid band for the colored carbinol as compared to the frequency of maximum absorption of the quinonoid band for the corresponding fuchsone is shifted toward the shorter wave lengths while in other cases it is shifted toward the longer wave lengths. The displacement of the peaks for the colored carbinols and the corresponding fuchsones is greater than the experimental error of determining the position of these peaks for the compounds indicated as a, c, d, f, g, h and i while for b and e the displacement is less than the experimental error. In a, h and i the peak for the fuchsone compared to that of the corresponding carbinol is displaced toward the shorter wave lengths, while in all the other groups the displacement is toward the longer wave lengths. These data allow an interesting observation to be made. When the groups in the ortho position to the nuclear hydroxyl are the same (a, h and i) the displacement of the peak for the quinonoid band of the colored carbinol compared to that of the fuchsone is toward the longer wave lengths. If the groups in the ortho position to the nuclear hydroxyl are not alike, then the displacement is in the opposite sense. It does not seem likely that this relation is due to chance, since no inconsistencies have been observed in any of the compounds studied.

The fact that the position of the quinonoid band for the colored carbinol and the quinonoid band for the corresponding fuchsone is not at the same

frequency is a positive indication that the colored carbinol is not the colorless carbinol with small amounts of fuchsone as impurity. The two effects, namely, the displacement of the quinonoid band for the colored carbinol as compared to that of the fuchsone and the lowering of the quinonoid absorption band of the colored form of 4-hydroxytriphenylcarbinol by a

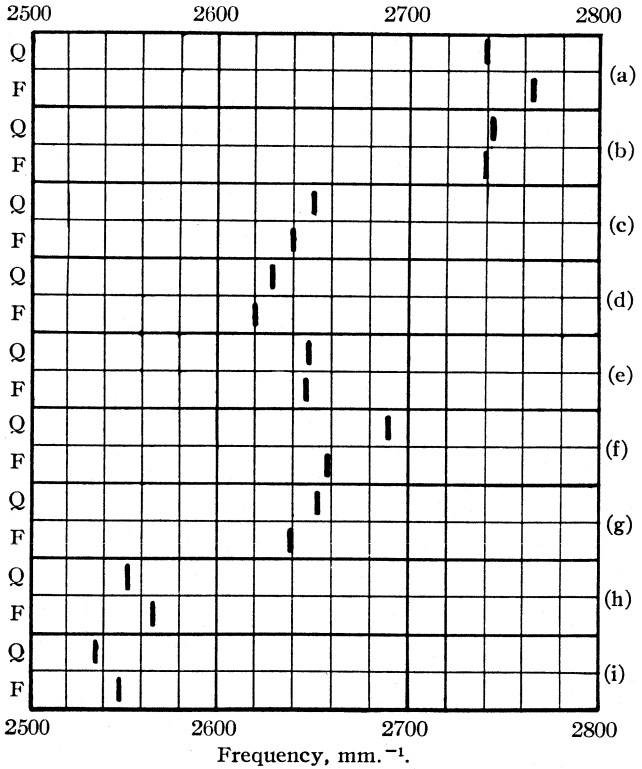


Fig. 5.—Q = colored carbinol; F = fuchsone: (a) 4-hydroxytriphenylcarbinol; (b) 3-methyl-4-hydroxytriphenylcarbinol; (c) 3-methyl-5-chloro-4-hydroxytriphenylcarbinol; (d) 3-methyl-5-bromo-4-hydroxytriphenylcarbinol; (e) 3-methoxy-4-hydroxytriphenylcarbinol; (f) 3-chloro-4-hydroxytriphenylcarbinol; (g) 3-bromo-4-hydroxytriphenylcarbinol; (h) 3,5-dichloro-4-hydroxytriphenylcarbinol; (i) 3,5-dibromo-4-hydroxytriphenylcarbinol.

definite amount, both of which phenomena occur when one and two of the hydrogens adjacent to the nuclear hydroxyl group are replaced, appear to be evidence in favor of the hypothesis that the ring in which the substitution has been made has a very direct influence upon the nature of the electron transition which produces this band and also upon the probability of the occurrence of this transition.

TABLE II

FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

	3-Cl-4-OH triphenyl	3-Br-4-OH triphenyl	3,5,Cl_2-4-OH triphenyl	3,5-Br_2-4-OH triphenyl
Methane	3449	3433	3414	3409
	3530	3516	3508	3502
	3704	3702	3700	3702
	3802	3802	3802	3804
	3901	3906	3897	3906
	4014			
Carbinol (colorless)		3463	3445	3436
		3548	3550	3532
		3715	3654	3633
		3770	3717	3715
		3865	3771	3770
		3960	3865	3866
			3963	3963
Carbinol (colored)	2690	2654	2552	2540
	3477	3463	3445	3430
	3558	3549	3547	3520
	3720	3644	3658	3639
	3771	3718	3720	3715
	3862	3770	3783	3786
	3958	3859	3864	3865
		3949	3956	3956
Carbinol fuchsone	2659	2639	2567	2550
	3713	3720	3701	3668

Experimental

The apparatus and the methods used for obtaining the quantitative absorption spectra as well as the methods employed for determining the frequencies of maximum absorption have been described.[2]

The four fuchsones studied in this investigation were each prepared according to the method of Gomberg and Van Stone.[4] They were all carefully crystallized from ether which showed no selective absorption between 2300 and 7500 Å. The four colored carbinols were prepared by adding hot water to a solution of the corresponding fuchsone in glacial acetic acid until the concentration of the acetic acid in the solution had been reduced to 60%. After allowing the mixture to cool the crystals were filtered off and dried in a vacuum desiccator over soda lime. Each of the three colorless carbinols was prepared by dissolving the corresponding fuchsone in normal alkali and treating the clear, cold solution with ammonium chloride. The precipitate was filtered off and crystallized from optically clear ether and hexane. The four methanes that were studied were prepared by reducing the corresponding fuchsone with zinc dust and glacial acetic acid. Each of them was crystallized from optically clear hexane. The melting points of the compounds prepared as described above are as follows (degrees centigrade):

		Carbinol		
	Methane	Colorless	Colored	Fuchsone
3-Chloro-4-hydroxytriphenyl	73		124–125	161
3-Bromo-4-hydroxytriphenyl	79	108.5–109	105–105.5	139.5
3,5-Dichloro-4-hydroxytriphenyl	105	132	133–134	216
3,5-Dibromo-4-hydroxytriphenyl	130	136	136–137	233

Summary

1. Curves have been prepared which show the quantitative absorption spectra of the methane, colored carbinol and fuchsone of each of the following compounds: 3-chloro-4-hydroxytriphenylcarbinol, 3-bromo-4-hydroxytriphenylcarbinol, 3,5-dichloro-4-hydroxytriphenylcarbinol and 3,5-dibromo-4-hydroxytriphenylcarbinol together with the curves for the colorless carbinols of the last three compounds.

2. Symmetrical or unsymmetrical substitution in the ortho positions to the nuclear hydroxyl group of 4-hydroxytriphenylcarbinol has been shown to have a definite effect upon the height of the quinonoid band for the colored carbinol; symmetrical substitution producing a greater absorption.

3. The direction of the displacement of the quinonoid band for the colored carbinol, in reference to the position for the quinonoid band for the corresponding fuchsone of the 4-hydroxytriphenylcarbinol series has also been found to be dependent upon the groups substituted in the ortho positions to the nuclear hydroxyl. If the two groups are the same the displacement is in one direction, while if they are different, the displacement is in the opposite direction.

ANN ARBOR, MICHIGAN

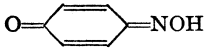
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE TAUTOMERISM OF QUINONEOXIME AND PARA-NITROSOPHENOL

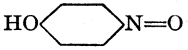
BY LEIGH C. ANDERSON AND M. B. GEIGER

RECEIVED FEBRUARY 8, 1932 PUBLISHED AUGUST 5, 1932

The chemical reactions and the methods of preparation of quinoneoxime (I) indicate that it is in tautomeric equilibrium with *p*-nitrosophenol (II); the relative amounts of the two substances present being dependent upon the solvent and conditions which are employed.



I



II

It has been generally accepted that the methyl ethers of tautomeric substances do not undergo tautomerization and that in many instances each can be obtained pure. A comparison of the physical properties of a solution of the tautomeric mixture of non-methylated substances with solutions of each of the corresponding methyl ether isomers has been used in investigations of compounds such as isatin, acetoacetic ester, etc., to determine the extent to which each of the tautomeric forms occurs in the equilibrium mixture. This procedure has been followed in the present investigation in the case of the mixture of quinoneoxime and *p*-nitrosophenol. Ether has been chosen as the solvent because it is optically

clear in the visible and ultraviolet regions, it is chemically inert toward solutes and also because all the compounds included in this work are monomolecular in this solvent. Sluiter[1] has shown that *p*-nitrosophenol, which is polymolecular in most solvents, is monomolecular in ether regardless of the concentration of the solution.

The methyl ethers of quinoneoxime (III) and of *p*-nitrosophenol (IV) have been described in the literature. A comparison of the quantitative absorption spectrum of the tautomeric mixture of quinoneoxime and *p*-nitrosophenol with that of each of the ethers should indicate which form is present to the greater extent. These curves are presented in Fig. 1. The similarity in the curves for quinoneoxime methyl ether and the tautomeric mixture is obvious. The absorption curve for *p*-nitrosoanisole differs from the curves of the other solutions in that it shows no indication of fine bands in the edge of the visible region and the band in the ultraviolet is much narrower.



III

IV

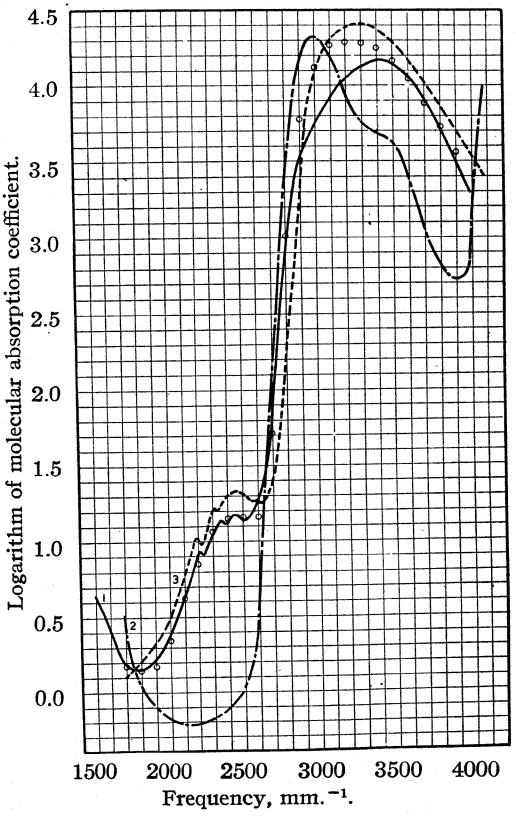


Fig. 1.—1, Tautomeric mixture of quinoneoxime and *p*-nitrosophenol; 2, *p*-nitrosoanisole; 3, quinoneoxime methyl ether.

The similarity of the curves for the tautomeric mixture and quinoneoxime methyl ether leaves no doubt that the mixture in ether solution is mainly in the quinoneoxime form. On the assumption that the curves for pure quinoneoxime and pure *p*-nitrosophenol should be similar each to the curve for the corresponding methyl ether, it is possible from Fig. 1 to make an estimate of the composition of the mixture. A comparison of the

[1] Sluiter, *Rec. trav. chim.*, **25**, 8 (1906).

quantitative absorption curves which are given in Fig. 2 for hydroquinone and its mono- and dimethyl ethers indicates that in these compounds the principal effect produced upon methylation is a displacement of the absorption toward the shorter wave lengths.

An examination of the curves in Fig. 1 shows that between frequencies 2000 and 2500 mm.$^{-1}$ the *p*-nitrosophenol tautomer should have little influence on the height of the curve of the mixture; and since curve 1 is about 70% as high as curve 3 within this region, the mixture should contain approximately 70% quinoxneoime and 30% *p*-nitrosophenol. Using values corresponding to such a mixture of methyl ethers and extending the calculations out to the regions where both compounds influence the absorption curve of the mixture, the values indicated by the circles in Fig. 1 are obtained. It will be seen that the agreement is very good except near the top of the absorption band in the ultraviolet. The disagreement within this region probably indicates that our assumption of the close similarity of the curves of the methyl ethers to the corresponding hydroxy compounds does not hold within these limits. Studies of solutions of this tautomeric mixture in other solvents are being carried on.

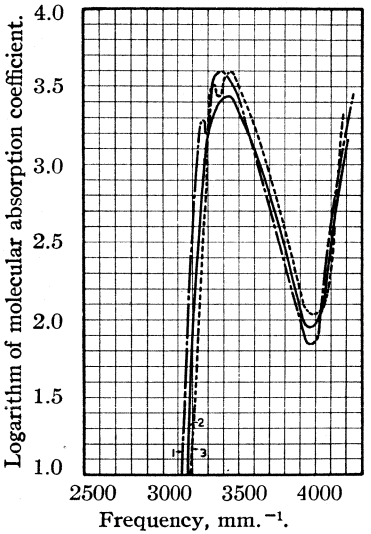


Fig. 2.—1, Hydroquinone; 2, hydroquinone monomethyl ether; 3, hydroquinone dimethyl ether.

The curves for the quantitative absorption spectra for quinone, quinonechlorimine and quinonedichlorodiimine are shown in Fig. 3, and the curves for quinone and quinonedioxime are shown in Fig. 4. In the latter figure a curve has been included for the absorption spectrum that we should expect to obtain from a sample of pure quinoneoxime. That portion of the curve has been omitted where the previously made assumptions do not seem to apply. The frequencies of maximum absorption for the bands in the visible which are indicated in Fig. 4 and in the table are the same as those found for quinoneoxime in the tautomeric mixture. The compounds in Fig. 3 are the derivatives of quinone in which the ketonic oxygen has been replaced by the =NCl group, and the compounds in Fig. 4 are the derivatives of quinone in which the ketonic oxygen has been replaced by the =NOH group.

The progressive changes which are noted on the successive substitution of the =NCl group for a =O group in quinone are the shifting of the ultraviolet band toward the visible and a shifting of the bands in the visible

region toward the ultraviolet. In quinonedichlorodiimine we find only one intense band. The ultraviolet band as we pass through the series successively persists over a greater dilution being least for quinone and greatest for quinonedichlorodiimine. In Fig. 4, similar changes are noted for the =NOH compounds. The curves for quinonechlorimine and the calculated one for quinoneoxime are very similar to each other, as are also the curves for quinonedioxime and quinonedichlorodiimine.

The quantitative absorption curves for the reduction products of each: quinone, quinoneimine and quinonediimine, namely, the curves for hydroquinone, *p*-aminophenol and *p*-phenylenediamine, are given in Fig. 5.[2] The solvent used was absolute ether. *p*-Aminophenol and *p*-phenylenediamine may be considered as derived from hydroquinone by

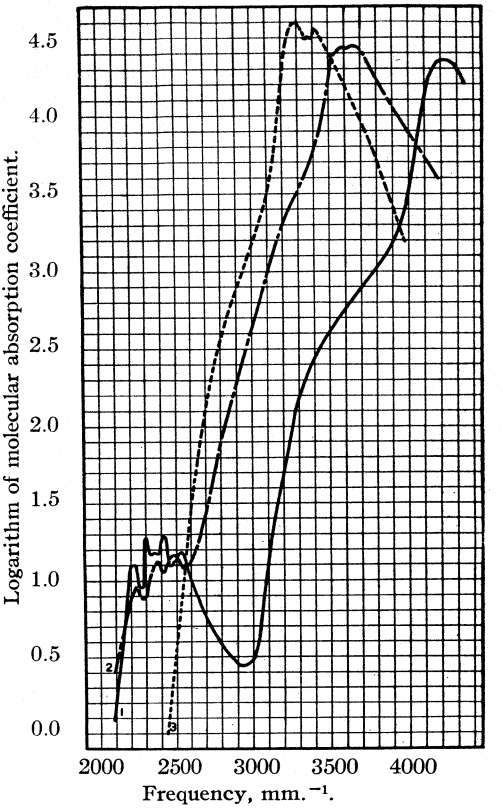


Fig. 3.—1, Quinone; 2, quinone chlorimine; 3, quinonedichlorodiimine.

FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

Quinoneoxime		2095	2210	2349	2456	3417		
Quinoneoxime methyl ether		2187	2301	2447	2575	3234		
p-Nitrosoanisole					2989	3493		
Hydroquinone					3270	3373		
Hydroquinone methyl ether						3415		
Hydroquinone dimethyl ether					3345	3436		
Quinone	2125	2200	2236	2317	2360	2429	3580	4123
Quinonedioxime					3212			
Quinonechlorimine	2155	2267	2380	3459	3557			
Quinonedichlorimine				3184	3260	3305		
p-Aminophenol				3228				
p-Phenylenediamine				3099				

[2] References to previous work upon the absorption spectra of quinone, its methyl ethers, hydroquinone, *p*-aminophenol and *p*-phenylenediamine may be found in Volume V of the "International Critical Tables."

the replacement of the hydroxyl groups of hydroquinone with amino groups. The regular changes in absorption curves which accompany these replacements are, first, a shifting of the absorption toward the visible region and, second, a decrease in its persistence.

The question of the structure of quinone and its derivatives has received considerable attention in the past. The assignment of the diketonic formula to quinone has been favored by evidence obtained by Garner and Sugden[3] from parachor measurements, by Pascal[4] from magnetic susceptibility measurements and by Light[5] from absorption spectra data. The most recent data which favor the peroxidic formula were presented by Binder[6] from heats of combustion. If the quinone derivatives are better represented by the peroxidic structure, then the general location and the height of the absorption bands of these derivatives should resemble those of hydroquinone and its derivatives, since under such an assumption, they would all contain a benzenoid nucleus. That there is, however, no such resemblance is evident from a comparison of the curves in Figs. 2 and 5 with those in Figs. 3 and 4. The compounds of known benzenoid structure of Figs. 2 and 5 have no absorption in or adjacent to the visible region of the spectrum and the absorption band in the ultraviolet is only about one-tenth as persistent as the ultraviolet band for the quinone derivatives. Our conclusion, therefore, is that the diketonic structure best explains the data obtained from the absorption spectra.

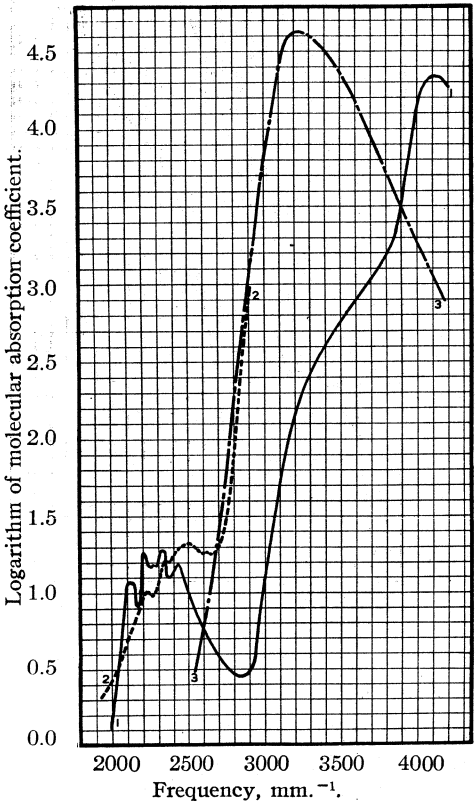


Fig. 4.—1, Quinone; 2, quinoneoxime (calcd.); 3, quinonedioxime.

[3] Garner and Sugden, *J. Chem. Soc.*, 2877 (1927).
[4] Pascal, *Bull. soc. chim.*, [4] **9**, 339, 812 (1911).
[5] Light, *Z. physik. Chem.*, **122**, 414 (1926).
[6] Binder, *Chem.-Ztg.*, **45**, 1114 (1921).

Experimental

The instruments and methods used for obtaining the quantitative absorption curves and points of maximum absorption have been described.[7] In the purification of all the compounds except quinone, *p*-aminophenol and *p*-phenylenediamine the final recrystallization was carried out from a solvent which showed no selective absorption between 2300 and 7500 Å. The material which on solution in ether produced the tautomeric mixture of quinoneoxime and *p*-nitrosophenol was prepared by the action of nitrous acid on phenol. The product was first crystallized from water using charcoal for decolorizing, and finally from ether; m. p. 128–129°.

***p*-Nitrosoanisole.**—*p*-Nitrosoanisole was reduced to the corresponding hydroxylamine and this compound was oxidized to the nitroso derivative by the method described by Rising.[8] The product was purified by distillation with steam and was crystallized from hexane; m. p. 22.5°.

Quinoneoxime methyl ether was obtained by the methylation of quinoneoxime with diazomethane.[9] It was crystallized from hexane; m. p. 82°.

***p*-Quinone** was prepared by the oxidation of hydroquinone with chromic acid. The crude product was purified by several successive sublimations; m. p. 116°.

Quinonechlorimine was obtained by the action of sodium hypochlorite on the hydrochloride of *p*-aminophenol.[10] The material was crystallized from hexane; m. p. 87°.

Quinonedichlorodiimine resulted from the oxidation of *p*-phenylenediamine hydrochloride with sodium hypochlorite.[10] The product was crystallized from hexane; m. p. 128° with decomposition.

Quinonedioxime was prepared by the action of hydroxylamine hydrochloride on quinoneoxime.[11] The material was crystallized from ether; m. p. 242° with decomposition.

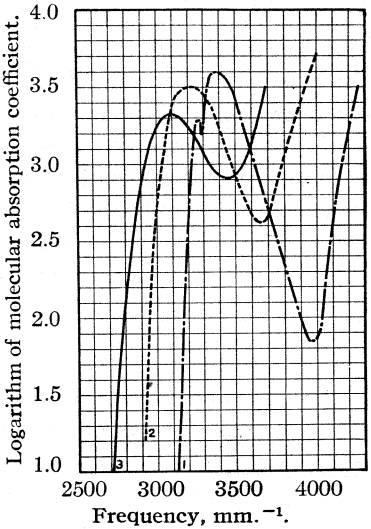


Fig. 5.—1, Hydroquinone; 2, *p*-aminophenol; 3, *p*-phenylenediamine.

Hydroquinone.—Kahlbaum's product was crystallized from water using charcoal for decolorizing; m. p. 169°.

Kahlbaum **hydroquinone monomethyl ether** was crystallized from hexane; m. p. 55.5°.

The **dimethyl ether of hydroquinone** was obtained by crystallizing an Eastman product from 95% alcohol; m. p. 56°.

Eastman ***p*-aminophenol** was purified by sublimation at 180° under reduced pressure (2 mm.); m. p. 184° with decomposition.

---

[7] Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928); Anderson, *ibid.*, **51**, 1889 (1929).

[8] Rising, *Ber.*, **37**, 44 (1904).

[9] Von Pechmann and Seel, *ibid.*, **31**, 299 (1898).

[10] Willstätter and Mayer, *ibid.*, **37**, 1498 (1904).

[11] Lobry de Bruyn, *Rec. trav. chim.*, **13**, 109 (1894).

Eastman's *p*-**phenylenediamine** was sublimed at 200° under reduced pressure (2 mm.); the pure white product melted at 140°.

Summary

1. The quantitative absorption curves for ether solutions of *p*-nitrosoanisole, the methyl ether of quinoneoxime and of quinoneoxime have been determined. The spectroscopic results indicate that quinoneoxime and *p*-nitrosophenol are in tautomeric equilibrium in ether solutions in the ratio of approximately seven parts of the former to three parts of the latter.

2. The quantitative absorption spectra of ether solutions of quinone, quinoneoxime, quinonedioxime, quinonechlorimine and quinonedichlorodiimine together with the curve for the tautomeric mixture of quinoneoxime, and *p*-nitrosophenol have been obtained. The conclusion is drawn from these data that the diketonic or quinonoid formula represents the correct structure for quinone and the quinone derivatives.

3. The quantitative absorption curves for the ether solutions of hydroquinone, *p*-aminophenol, *p*-phenylenediamine, hydroquinone monomethyl ether and hydroquinone dimethyl ether have been obtained.

4. The frequencies of maximum absorption for all the compounds studied in this investigation have been ascertained and these values are presented in a table.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. IX. REACTIONS BETWEEN PERSULFIDES OF HYDROGEN AND ORGANIC COMPOUNDS

BY WALTER BERNARD KING[1] AND JOHN A. WILKINSON

RECEIVED FEBRUARY 23, 1932 PUBLISHED AUGUST 5, 1932

The persulfides of hydrogen bear the same relationship to liquid hydrogen sulfide as does hydrogen peroxide to water. Since hydrogen sulfide dissolves organic bodies very readily, more readily than does water, one would expect that the hydrogen persulfides would react with organic compounds more readily than does hydrogen peroxide but in a similar manner.

Up until the work of Bloch and Höhn,[2] Schenck and Falcke[3] and Brunner and Vuillenmuir[4] the properties of the hydrogen persulfides were either little known or the data given were incorrect.

The reactions of hydrogen peroxide on organic compounds were in-

[1] This work is from a portion of a thesis presented to the Graduate Faculty of Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bloch and Höhn, *Ber.*, **41**, 1961–1980 (1908).

[3] Schenck and Falcke, *ibid.*, **41**, 2600 (1908).

[4] Brunner and Vuillenmuir, *Schweiz. Med. Wochschr.*, **46**, 436 (1908).

vestigated by Fenton[5] and Walton and Jones,[6] who showed that in the presence of ferrous salts the following reactions took place with hydrogen peroxide. Glycolic acid is changed to glyoxylic acid, tartaric acid to dihydroxymalic acid, primary amines to aldehydes, piperidine to glutaric acid, benzene to phenol, benzonitrile to benzamide, azo compounds to azoxy compounds and phenol to dihydroxyphenol or quinone.

It will be noticed that all of the above reactions are of an oxidizing nature, either removing hydrogen or adding oxygen. Walton and Jones[6] also showed that substances which will catalyze reactions of hydrogen peroxide in water solution will catalyze similar reactions in organic solvents.

In endeavoring to duplicate similar reactions with persulfides, alkaline solutions cannot be used because alkalies will decompose the persulfides very rapidly. Catalysts such as ferrous salts cannot be used because the persulfides are decomposed by them. Walton and Parsons[7] showed that the persulfides are decomposed by many oxides and inorganic salts. It was found, however, that solutions of the persulfides in organic solvents without catalysts could be used in bringing about similar reactions.

Experimental

Preparation of the Persulfides.—The persulfides were prepared by the method of Walton and Parsons[7] by heating a mixture of sodium sulfide and sulfur and water for several hours on a water-bath. The flask containing the mixture was closed with a Bunsen valve to prevent the entrance of air. This made it unnecessary to pass hydrogen through the solution during the heating. The solution of the sodium persulfide thus formed was allowed to run beneath the surface of concentrated hydrochloric acid kept at a temperature of -10 to $-4°$. As soon as a brown film started to form on the surface of the acid, showing that the persulfides were beginning to decompose, a fresh supply of acid was used. An emulsion of the persulfides was first formed which settled after several hours to form a yellow liquid. This was washed with distilled water in a separatory funnel and dried over phosphorus pentoxide. The material thus obtained is a mixture of the di- and the trisulfides and these may be separated and purified by fractional distillation in quartz apparatus as described by Walton and Parsons. The yield of the trisulfide obtained in this way was about 10% of the total crude persulfides. The crude persulfide mixture and the pure trisulfide react in the same manner so that in most of the work only the crude material was used.

Reactions of Liquid Hydrogen Sulfide on Styrene and Amylene.—Ten grams of each of these two bodies were sealed in glass tubes with four cubic centimeters of liquid hydrogen sulfide at the temperature of an ether–solid carbon dioxide bath, and allowed to come to room temperature and stand for two weeks. In neither case was any reaction apparent. When the hydrogen sulfide was allowed to evaporate, the styrene and amylene were recovered unchanged. This shows the stability of these two unsaturated bodies toward liquid hydrogen sulfide and indicates that any reduction or oxidation brought about by the persulfides could not be due to the hydrogen sulfide formed by the decomposition of the persulfide.

[5] Fenton, *J. Chem. Soc.*, **65**, 899 (1894); **67**, 774 (1895).

[6] Walton and Jones, THIS JOURNAL, **38**, 1956 (1916).

[7] Walton and Parsons, *ibid.*, **43**, 2546 (1921).

Reaction of Hydrogen Persulfides with Styrene.—To find the effect of the persulfides on a double bond between two carbon atoms styrene was treated with some of the crude persulfide. Twenty grams of the crude sulfide was added to forty grams of styrene dissolved in 180 cc. of benzene. The mixture became warm and was colored first yellow and then green and finally became milky. After standing for a few hours the mixture was refluxed at the temperature of boiling benzene for six hours. Upon cooling, crystals of sulfur were precipitated, leaving a clear yellow solution. Ammonia gas was passed through the solution for five minutes and a heavy orange precipitate was formed. This was filtered off and discarded and the benzene removed from the filtrate by vacuum distillation. The liquid residue, weighing 42 g., was purified by dissolving in ether and passing ammonia gas into this solution until no more sulfur precipitated. The sulfur was filtered out and the ether evaporated, leaving a clear light yellow liquid. This was heated in a water-bath under a pressure of 30 mm. to remove any unchanged styrene. The ether solution could be changed into a wine colored one by passing ammonia gas into it but no sulfur could be precipitated. The yellow color would return to the solution if either air or illuminating gas was passed into the solution to remove the ammonia. A similar product may be made by adding pure styrene to the persulfide without the addition of a solvent providing the temperature is kept below 40°. An analysis of the liquid for the sulfur content showed 37.44 and 37.40% while the calcd. for the compound $C_6H_5—CH(S—S)—CH_2$ is 38.12% and for the compound $C_6H_5—CH(S)—CH_2$ is 23.55%. Bloch, Höhn and Bugge[8] reported a similar compound but their analysis for the percentage of sulfur was much lower (29.8). This is probably due to the use of $(NH_4)_2S$ in dissolving out the excess of sulfur instead of precipitating it with ammonia gas. Undoubtedly some of their compound was decomposed and part of the sulfur they removed came not from free sulfur but from the chemically combined sulfur.

The material could not be distilled as it decomposes to give styrene and sulfur. It does not add bromine and is stable toward hypochlorites and alkalies. Concentrated nitric acid oxidizes it completely to water, carbon dioxide and sulfuric acid. A molecular weight determination gave a value of 252, showing that some polymerization had occurred. The persulfide in this reaction has acted as an oxidizing agent, adding sulfur at the double bond. There was no evidence of there being any reducing action to form ethylbenzene.

Reaction of the Persulfides with Amylene.—As another compound containing a double bond between two carbon atoms amylene, the unsymmetrical methylethylethylene, was used. Both the pure trisulfide and the crude mixture of the persulfides gave the same reaction with the body.

Ten grams of the pure trisulfide was added to 50 cc. of amylene. No reaction took place at first but after a few hours standing a compound with an odor similar to a mercaptan was formed. After a week the crystals of sulfur which had formed were filtered off and the greenish yellow liquid was heated in a water-bath under a vacuum but nothing was distilled over. When the liquid was treated with ether, sulfur was precipitated in a large amount. On passing ammonia gas into the ether solution a colloidal orange precipitate formed which after standing for several days settled to a clear liquid with a strong odor of a mercaptan. After removing the ether the light yellow liquid did not add bromine, and was stable toward hypochlorites, alkalies and dilute acids. An analysis of this liquid for the per cent. of sulfur showed 45.38 and 44.84 while the theoretical for the compound $C_5H_{10}S$ is 31.37% and for $C_5H_{10}S_2$ is 47.76%. The boiling point of the liquid is 132–135° under a pressure of 8 mm. although different preparations of the liquid vary

[8] Bloch, Höhn and Bugge, *J. prakt. Chem.*, **82**, 473–485 (1908).

some from this. The liquid is probably not entirely pure but contains some of both the mono- and di-sulfur compound. Here again the action of persulfides is one of oxidation or addition of sulfur at the double bond.

Reaction of the Persulfides with Azobenzene.—As hydrogen peroxide forms azoxybenzene from azobenzene the similar reaction between the persulfides and azobenzene should give a thioazoxybenzene. When benzene solutions of the persulfides and the azobenzene were mixed, no reaction was apparent for an hour. After standing for three hours and then refluxing at the temperature of boiling benzene for twenty minutes and cooling, crystals of sulfur were deposited. The sulfur was filtered out and the benzene removed by distillation. The solid residue was purified by recrystallizing several times from 95% ethyl alcohol. The crystals thus obtained melted at 126° and a mixed melting point determination showed it to be hydrazobenzene. No sulfur was added at the double bond as in the case of the peroxide on azobenzene.

Reaction of the Persulfides with Benzenediazonium Chloride.—In order to observe the effect of the persulfides on a triple bond between two nitrogen atoms the compound benzene diazonium chloride was used. If the dry material is added to the liquid persulfide at room temperature the reaction is of explosive violence. If the solid is cooled and the sulfide added slowly the reaction is somewhat slower and by dissolving in either carbon disulfide or benzene it becomes quite mild. From a carbon disulfide solution a large amount of hydrogen chloride is liberated, a red liquid forms, and a buff colored solid with the odor of a mercaptan remains. This solid is explosive on heating, showing that some of the diazonium compound still remains unacted upon. The difficulty in studying this reaction is in finding some medium which will dissolve both the persulfide and the diazonium chloride. The former dissolves quite readily in organic solvents but the latter being of the nature of a salt is insoluble in such solvents. This reaction is being studied further.

Conclusions

1. While liquid hydrogen sulfide does not react with either styrene or amylene the persulfides do react, adding the group —S—S— at the double bond. This reaction is essentially one of oxidation similar to the action of hydrogen peroxide.

2. The persulfides form hydrazobenzene from azobenzene, which is essentially a reducing reaction and differs from the reaction with hydrogen peroxide.

3. With diazonium chloride the reaction with the persulfides is so vigorous that it takes place with explosive violence unless it can be regulated by the use of a solvent such as carbon disulfide.

AMES, IOWA

[CONTRIBUTON FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

AN ESTIMATION OF SOME SPECTRAL PROPERTIES OF ELEMENT 87

BY HERMAN YAGODA*

RECEIVED MARCH 4, 1932 PUBLISHED AUGUST 5, 1932

Evidence for the existence of minute quantities of element 87 in several alkali-bearing minerals has recently been secured by Allison and his collaborators[1] using the magneto-optic method of analysis, and also by Papish and Wainer[2] through x-ray analysis of a concentrate from the mineral samarskite. The latter investigators have questioned the evidence adduced from the magneto-optic analyses, claiming that the minima attributed to the missing alkali element are also given by certain complex ions, as $SnCl_3^+$ and $ReCl^+$. More refined measurements of the position of the minima by McGhee and Lawrenz[3] and by Allison and his collaborators[4] reveal that a conflict between the points used to identify element 87 and those given by the complex ions is not probable.

The delicacy of spectroscopic analysis is well known, and the fact that two homologs of element 87, rubidium and cesium, were first discovered in that way by R. Bunsen and G. Kirchhoff suggests that the spectroscopic method of analysis may also prove useful in establishing the existence of the element in question. The several investigators[2,5] who have approached this problem placed little weight on the negative results obtained from their spectroscopic analyses, claiming that the spectral lines of the principal series are located in the far-red end of the spectrum where visual and photographic sensitivity are very poor. It is true that by extrapolating a wave length–atomic number function through potassium, rubidium and cesium, a value for the first transition is obtained that locates the line in the red end of the spectrum, but such an extrapolation, as will soon be shown, is not justified. Furthermore, in the practical detection of traces of potassium, rubidium and cesium, the second transition of the series is used for the identification of the element, as the respective lines reside in the violet region of the spectrum where photographic sensitivity is close to its maximum value.

The present writer has shown that the 1^2S-3^2P_2 transition has an approximate wave length of 4260 Å. This value was obtained through the use of an empirical observation that the quantum defect of a given elec-

* Formerly a fellow at the University.

[1] Allison and Murphy, *Phys. Rev.*, **35**, 285 (1930).

[2] Papish and Wainer, THIS JOURNAL, **53**, 3818 (1931).

[3] McGhee and Lawrenz, *ibid.*, **54**, 405 (1932).

[4] Allison, Bishop, Sommer and Christensen, *ibid.*, **54**, 613 (1932).

[5] Meggers, *Science Supplement*, **74**, 10 (1931).

tronic level (Q) in a sequence of homologous elements is approximately a linear function of the total quantum number (n) of the valence electron.[6] Data are lacking by which this figure can be directly compared, but its validity can be partially tested by the ionization potential predicted by the same method, as the latter can be calculated from several independent considerations.

It is generally known that in the periodic classification of the elements the properties of the members of the second and fourth periods exhibit anomalous behavior when the properties of a given group of elements are considered. The question arises whether members in the seventh period, and element 87 in particular, are also exceptions to the rule governing the properties of the group. The writer has been interested in this problem for some time, as it is of practical importance in developing a method for the concentration of the missing element.[7] The chief evidence available for the solution of this problem resides in the measurements of the optical spectrum of radium and its analysis into terms by Hicks.[8] When the spectral properties of RaII are compared with those of the other alkaline earths, it is observed that the wave lengths of the first two transitions are anomalous with respect to the similar lines of calcium, strontium and barium, and that both the ionization potential and the doublet separation of the first transition exhibit marked departures from the relations connecting the respective properties of the other alkaline earth elements. Such an exceptional behavior might be expected from the intrusion of the rare-earth elements in the sixth period. In formulating a relationship between the ionic potential and the ionization potential, Cartledge[9] has shown that for ions of only slightly larger size than cesium and barium, unusual behaviors can be expected owing to the great polarizing effect of the valence electron upon the ion. It is highly probable that the spectroscopic properties of element 87 will not follow the same trend as the triad, potassium, rubidium and cesium, and that any theoretical or empirical method which permits the correct prediction of the known properties of the singly ionized radium atom may also furnish a correct guide to the unknown properties of the neutral eka-cesium atom.

Table I represents a summary of the different methods employed in the estimation of the probable ionization potential of element 87. The first value was calculated from deductions made by Fermi[10] concerning the

[6] Yagoda, *Phys. Rev.*, **38**, 2298 (1931).

[7] "Investigation of a Pollucite Ore for the Detection of Eka-cesium," H. Yagoda, dissertation at New York University (June, 1931). I wish to take the opportunity here, of expressing my indebtedness to Prof. H. M. Partridge for suggesting this problem to me.

[8] "International Critical Tables," Vol. V, 1929, p. 392; W. M. Hicks, "Analysis of Spectra," Cambridge, 1922, p. 276.

[9] G. H. Cartledge, THIS JOURNAL, **52**, 3076 (1930).

[10] Fermi, *Z. Physik*, **49**, 550 (1928).

quantum defects of the S levels of the elements as a function of their atomic number (N). Since Q is known, the value of the normal term can be calculated from the relationship

$$\nu = RZ_0^2/(n - Q)^2$$

where ν represents the wave number of the level, R the Rydberg constant and Z_0 the mean effective nuclear charge for the outer portion of the electronic orbit. For the element in question, $\nu = (109{,}680 \times 1^2)/(7 - 5.22)^2 = 34{,}600$, and the ionization potential, $V = \nu/8106 = 4.27$ volts.

Cartledge[9] has shown that V can be calculated from the ionic potential (φ); this leads to a value of 4.55 volts. In a private communication Cartledge states: "This extrapolation value is in error, both on account of the disturbances introduced by the abnormally great polarizability of the seventh-period ions, and because of the uncertainty of the radius of the Ra^{++} ion."[11] From the several estimates of the radius, Cartledge finds that a probable value of the ionization potential resides between 4.2 and 4.4 volts.

The ratio of corresponding alkali and alkaline earth terms is nearly a constant for all the family members. The logarithm of this ratio plotted against n gives a smooth curve which can be extrapolated for the particular value of Eka-CsI/RaII with a fair degree of accuracy; for the 1^2S term this ratio is equal to 0.399. The value of 4.05 volts published by Bainbridge[12] was probably obtained by a similar calculation.

Hume-Rothery[13] has recently demonstrated from considerations of the interatomic distance between atoms in metallic crystals that n^2V is a linear

TABLE I

IONIZATION POTENTIAL AND 1^2S TERM OF ELEMENT 87

Method	V	1^2S in ν	Quantity directly estimated
Statistical mechanics[10]	4.27	34,600	Q from N
Ionic potentials	4.3	34,900	φ from Ra^{++} data
Ratio Eka-CsI/RaII levels	4.09	33,100	Log of term ratios
Quantum defect rule	4.06	32,900	Q from n
Isoelectronics of radium[12]	4.05	32,800	
$n^2V = aN^{2/3} + b$	3.89	31,500	V from N and n
Atomic volume relationships	3.77	30,600	V from v and n
Probability numbers [14]	3.58	29,010	1^2S from N
Weighed average	4.11	33,320	Last two values excluded

function of $N^{2/3}$. On testing this relationship, the writer has found that for the neutral alkali atoms n^2V actually varied with the 0.6664 power of

[11] Cartledge, THIS JOURNAL, **50**, 2855 (1928).

[12] Bainbridge, *Phys. Rev.*, **34**, 752 (1929).

[13] Hume-Rothery, *Phil. Mag.*, [7] **11**, 670 (1931); [7] **13**, 196 (1932); Yagoda, *ibid.*, [7] **13**, 1163 (1932).

[14] Loring, *Chem. News*, **140**, 178, 202, 242 (1930); **143**, 18, 98, 149 (1931).

N, which is in very good agreement with the theoretic deduction, but that for the singly ionized atoms of the alkaline earth elements much better agreement with the observed data is obtained by using the relationship

$$\log n^2V = 0.6188 \log N + 1.4667$$

In both families, however, the first members, lithium and beryllium, show marked departures from these relationships, and when the above equation is extrapolated for V of RaII a value of 9.53 volts is obtained, whereas the constant calculated from the spectrum of the element is equal to 10.32 volts. The value of 3.89 volts estimated for element 87 from the relationship

$$n^2V = 9.836\ N^{2/3} - 2.580$$

is probably also too low.

The atomic volume of eka-cesium can be estimated from the observation made by Hicks[15] that in the alkali family the atomic volume (v) is expressed by the product of a constant k, and an integer s characteristic of the element. At 20°, $v = 11.5 \times 7 = 80.5$ cc. For the alkalies, the present writer has found that the ionization potential is connected with the atomic volume by the relationship $Vv^{1/4} = K$, where K is equal to 11.3 at 20°. These relationships indicate that the ionization potential of the element is 3.77 volts. However, lithium is a marked exception to both generalizations, hence the validity of the estimates for v and V for eka-cesium is also questionable. The lowest value of the ionization potential is that published by Loring;[14] this was secured by extrapolation of the 1^2S levels through all the alkalies.

In the alkaline earth spectra V diminishes progressively from beryllium to barium, but the value for radium is anomalous, being greater than that of barium. Therefore, the ionization potential of eka-cesium will probably also be greater than that of cesium. Of the values calculated, those numerically less than 3.88 volts (which is the ionization potential of cesium) have but little significance. The average of the estimates above 3.88 volts is 4.11 ± 0.2 volts. The particular value of V calculated from the quantum defect rule, 4.06 volts, is in good agreement with the average value.

Doublet Separations.—Each transition of the principal series spectra of the alkali atoms consists of two members of which the line of shorter wave length is the more intense, and in which the distance between the lines increases progressively from lithium to cesium. The separation of the lines in the first and second doublets is an important criterion in the spectro-

[15] Hicks, *Proc. Roy. Soc.* (London), **83**, 226 (1910). Recently, W. Biltz has shown that the atomic volumes of the elements at the absolute zero (v_0) are expressed by the relationship, $v_0 = 11.3\ n/Z_0$, where Z_0 is the periodic group number of the element. In many cases Hicks' integers (s) are identical to n; *Z. physik. Chem.*, Bodenstein Festband, 198 (1931); also, W. Biltz and K. Meisel, *Z. anorg. Chem.*, **198**, 191 (1931).

scopic identification of the alkali element in question. Bell[16] has demonstrated that for the known alkali atoms the doublet separations are expressed by the following equations:

2^2P_j: $\log \Delta\nu = 2.1515 \log N - 0.9997$; when $N = 87$, $\Delta\nu = 1490$
3^2P_j: $\log \Delta\nu = 2.160 \log N - 1.500$; when $N = 87$, $\Delta\nu = 490$

In view of the unusual relationships existent in the seventh period, I have thought it desirable to test similar equations on the alkaline earth family in order to judge how well they predicted the doublet separations of the singly ionized radium spectrum.

2^2P_j: $\log \Delta\nu = 1.925 \log N - 0.134$; when $N = 88$, $\Delta\nu = 4040$
3^2P_j: data are available only for the BeII and MgII spectra

The observed doublet separation in the case of radium is 4857.2ν. The above expressions, therefore, need modification in order to account for members of the seventh period. When corrective terms are introduced into Bell's expressions, their general precision is lost, but the range of extrapolation is improved.

Alkaline earth II spectra, 2^2P_j: $\log \Delta\nu = 1.537 \log (N - n^2) + 1.228$; when $N = 88$, $\Delta\nu = 4710$
Alkali I spectra, 2^2P_j: $\log \Delta\nu = 1.543 \log (N - n^2) + 0.771$; when $N = 87$, $\Delta\nu = 1620$

By extrapolating the ratio of the doublet separations of corresponding alkali and alkaline earth atoms a value of 1660ν is obtained for the 2^2P_j separation of element 87. Bainbridge[12] finds that this value is equal to $1675 \pm 50\nu$. It would seem then, that the separation of the first doublet is in the region of 1650ν.

However, a much larger value is obtained by applying the Landé relationship[17]

$$\Delta\nu = \frac{R\alpha^2 Z_0^2 Z_i^2}{(n^*)^3 l(l+1)} \left[1 + \frac{5}{8}(\alpha Z_i)^2 + \frac{53}{128}(\alpha Z_i)^4 + \ldots\right]$$

Here α represents the fine structure constant $2\pi e^2/hc$, n^* and l the effective and azimuthal quantum numbers, and Z_i the effective nuclear charge for the inner portion of the electronic orbit. For the first transition of the singly ionized radium spectrum, $Z_i = 83.6$, $n^* = 2.784$, $Z_0 = 2$, $l = 1$ and $\alpha = 0.007284$.[18] These quantities lead to a value of 4860ν, which is in excellent agreement with the observed doublet separation. In order that the Landé formula be applicable to the spectrum of element 87, n^* and Z_i for the 2^2P_2 and 3^2P_2 levels must be known. The mean value of n^* for the 2^2P_2 level is 2.365.[19] Landé has shown that Z_i differs only by a small

[16] H. Bell, *Phil. Mag.*, [6] **36**, 337 (1918). The coefficients of the following two equations have been revaluated to fit more recent measurements of the doublet separations.

[17] Landé, *Z. Physik*, **25**, 46 (1924).

[18] Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

[19] This number was obtained by calculation from the mean of the two estimates available for the 2^2P_2 level of eka-cesium, *viz.*, Bainbridge[12] finds $19{,}670\nu$, and from the quantum defect rule[6] $19{,}540\nu$.

quantity from the atomic number of the atom. The screening constant (σ) is larger for an alkali atom than for the corresponding alkaline earth atom, the ratio of the two being 1.45 for the heavy atoms; also σ for RaII is less than that of BaII. The screening constant for the neutral eka-cesium atom should therefore be smaller than that of the neutral cesium atom, and be about 1.45 times as large as that of the singly ionized radium atom. A value of 6.4 satisfies these conditions; hence $Z_i = 80.6$, and $\Delta\nu$ for 2^2P_2 is equal to 1810ν. Assuming that Z_i for the second doublet is approximately the same as for the first, and that the value of 3^2P_2 is 9416ν,[6] then the displacement of the doublet in the violet region, as given by the Landé formula, is 600ν.

Now, the ratio of the displacements of the first and second doublets in the spectra of the neutral alkali atoms is nearly a constant for the group, and in the case of element 87 the ratio is probably 3.07. Dividing the average displacement of the first doublet, as found by the empirical relationships, by this figure gives as the displacement of the second doublet $1650/3.07 = 538\nu$. It can be assumed, then, that the distance between the two lines characterizing the doublet in the violet region is approximately $570 \pm 30\nu$. The average displacement for the first doublet is $1690 \pm 100\nu$.

Of the two lines constituting the doublet, the line of shorter wave length is the more intense. From the sum rule of Burger and Dorgelo[20] it may be expected that in the first doublet the major line will be twice as intense as the component of longer wave length; and from the empirical relationship formulated by Sambursky[21] it may be conjectured that in the second doublet the major line will be 8–9 times more intense than its satellite.

By correlating the limit of spectroscopic detection with the sensitivity of the recording device for the wave length and intensity of the light emitted on the return of electrons from the several energy levels to the alkali ions when the salts are dissociated in a flame at 2000°K., it can be deduced that about 10^{-5} g. of eka-cesium will be sufficient for the visual observation of the most persistent line in the red end of the spectrum[22] and that it will also suffice to record a photographic image of the *raie ultime* in the violet region. Experiments on the spectrophotographic detection of minute traces of potassium, rubidium and cesium in the presence of large amounts of the other elements reveal that the simultaneous

[20] Burger and Dorgelo, *Z. Physik*, **23**, 258 (1924).

[21] Sambursky, *ibid.*, **49**, 731 (1928).

[22] The wave length of the most persistent line in the red has been estimated at 7460 Å.;[6] Bainbridge[12] assigns to it a value of 7600 Å. H. Deslandres, *Compt. rend.*, **191**, 169 (1930), has observed that the constant $d = 1062.5\nu$ enters into the wave number relationships of the *raies ultimes* of the elements. Using a multiple of 13 (selected with the aid of the measured spectrum of radium) for element 87, a value of 7240 Å. is obtained for this line.

presence of the other ions in the flame does not appreciably affect the photographic sensitivity for the *raies ultimes* of the alkalies, and that, in particular, a thousand-fold concentration of sodium does not interfere with the spectrophotographic detection of 10^{-5} g. of potassium, rubidium or cesium.[23]

Allison states that the concentration of element 87, in the several minerals investigated, varies between 1 part in 10^{10} and 10^{8} parts of the mineral.[4] From the above deductions, it may be concluded that in order to secure spectroscopic evidence for the existence of element 87 a concentrate from 1–100 kg. of ore will be necessary, the quantity depending upon the nature of the mineral.

Summary

The ionization potential and the doublet separations of the principal series spectrum of element 87 have been evaluated by several independent methods. The values are not very concordant, but it may be assumed for purposes of further investigation that the ionization potential is approximately 4.11 ± 0.2 volts. In the spectrophotographic detection of the element, an intense line of approximate wave length 4260 ± 100 Å. is to be expected, followed by a much weaker line, of longer wave length, separated from the intense line by 550 ± 50ν.

[23] These experiments were performed in the Chemistry Laboratories of the Washington Square College, New York University, during the summer of 1931.

NEW YORK CITY, N. Y.

[CONTRIBUTION NO. 89 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

NON-METALLIC CATALYSTS FOR HYDROGENATION AND DEHYDROGENATION. II. THE CATALYTIC PROPERTIES OF CHROMIUM OXIDE

BY WILBUR A. LAZIER AND J. V. VAUGHEN

RECEIVED MARCH 8, 1932 PUBLISHED AUGUST 5, 1932

In the first report on the specificity of oxide hydrogenation catalysts[1] it was pointed out that a number of difficultly reducible oxides catalyze the hydrogenation of carbon monoxide and other compounds containing the carbonyl group, but are quite inert toward activating ethylene and its homologs for hydrogenation. A continuation of this line of investigation has led to the discovery that amorphous chromium oxide constitutes an exception to the rule governing the behavior of oxide catalysts generally. In fact, the high activity of specially prepared samples of chromium oxide as catalysts for the hydrogenation of ethylene prompted a further study of the catalytic properties of this oxide and the effect of variations in the

[1] Vaughen and Lazier, THIS JOURNAL, 53, 3719 (1931).

method of preparation, composition, physical condition and heat treatment.

Sabatier[2] lists chromium oxide as a catalyst of mediocre activity for the dehydrogenation and dehydration of alcohol, with the latter reaction predominating. Several other investigators have tested it alone and with zinc oxide as a catalyst for the synthesis of methanol.[3]

Hydrogenation of Ethylene and other Alkenes.—Attention was directed to the unique behavior of chromium oxide during a series of experiments in which hydrogenation occurred when a mixture of ethylene and hydrogen was passed over zinc oxide–chromium oxide catalysts of the type employed for methanol synthesis.[4] These catalysts were prepared by the thermal decomposition of zinc ammonium chromate containing a slight excess of chromic acid. The hydrogenating activity was at first attributed to the possible presence of small amounts of some contaminating oxide capable of yielding a metal on reduction with hydrogen. The same result, however, was obtained with chromium oxide prepared by the ignition of carefully purified ammonium bichromate. Chromium oxide was also prepared by precipitation in order to eliminate the reducing action of the ignition process as a factor in the development of catalytic activity. The use of a catalyst prepared by reducing chromic acid with methanol, followed by precipitation with ammonium hydroxide, led to the fullest manifestation of catalytic activity. These and subsequent experiments have fully established the fact that capacity for catalyzing the hydrogenation of simple alkenes is an inherent property of amorphous chromium oxide.

Extensive use has been made of the hydrogenation reaction as a control method for the investigation of the influence of variables of catalyst preparation and treatment on the catalytic activity. Comparison has been made of the relative efficiency of catalysts prepared from various salts by the use of several different precipitating agents. The effect of heating the catalysts in oxidizing and reducing atmospheres has been investigated. A résumé of representative results on the hydrogenation of ethylene is presented in Table I. In every case a 20-cc. sample of catalyst was heated to 400° in a slow current of hydrogen and held at this temperature while a 7-liter sample of an equimolar hydrogen–ethylene gas mixture was passed over the catalyst in an hour.

The first five runs shown are for chromium oxides prepared by igniting ammonium bichromate. This familar exothermic reaction, resulting in

[2] Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 252.

[3] See especially Huffman and Dodge, *Ind. Eng. Chem.*, **21**, 1056 (1929); Cryder and Frolich, *ibid.*, **21**, 867 (1929).

[4] Lazier, U. S. Patent 1,746,783, Feb. 11, 1930.

TABLE I

HYDROGENATION OF ETHYLENE OVER CHROMIUM OXIDE AT 400°

Run no.	Catalyst no.	Composition and preparation of catalyst	Comp. of entrance gas, % H_2	C_2H_4	C_2H_6	Volume change, %	Ethylene conversion, %	C_2H_6 in exit gas, %
1	1	Residue from ignition of $(NH_4)_2Cr_2O_7$ in deep vessel	56.9	40.7	1.9	− 0.7	2	1.6
2	2	Residue from ignition of $(NH_4)_2Cr_2O_7$ in thin layers	50.6	46.9	1.5	−37.3	80	65.0
3	3	$(NH_4)_2Cr_2O_7$ heated in vacuum to 245°	51.0	49.0	0.0	−12.3[a]	25	16.7
4	4	$(NH_4)_2Cr_2O_7$ heated in vacuum to 500°	50.0	50.0	.0	− 1.4[b]	3	3.7
5	3	Catalyst used in Run 3 heated in H_2 (thermal effect)	50.0	50.0	.0	− 1.9[b]	4	..
6	5	Chromium chromate (thermal effect during heating up)	49.5	50.5	.0	− 1.9[b]	4	..
7	6	Cr_2O_3 (by ignition of the oxalate)	50.0	50.0	.0	0.0	0	..
8	7	Cr_2O_3 (by ignition of the nitrate)	50.0	50.0	.0	0.0	0	..
9	8	Chromium hydroxide (*ex*-chromate reduced in HCl soln.)	51.0	49.0	.0	−36.2	74	65.0
10	9	Chromium hydroxide (*ex*-chromate reduced in H_2SO_4 soln.)	46.8	51.2	1.3	−41.0	80	77.1
11	9A	Duplicate of Catalyst 9	51.0	49.0	0.0	−43.2	88	62.4
12	10	Chrome gel (precipitated with NH_4OH from C. P. chloride)	52.5	47.5	.0	−36.0	76	54.0
13	11	Chrome gel (precipitated with NH_4OH from C. P. nitrate)	52.0	48.0	.0	−41.3	86	68.0
14	11A	Duplicate of Catalyst 11 (reduced in H_2 overnight at 400°)	49.0	51.0	.0	−43.5	85	81.0[c]
15	12	Chrome gel (precipitated with NaOH from chrome alum)	50.5	49.5	.0	−13.0	26	18.0
16	13	Chrome gel (precipitated with Na_2CO_3 from C. P. nitrate)	50.5	49.5	.0	−15.2	31	17.0[d]
17	14	Chrome gel (precipitated with KOH from C. P. chloride)	51.5	48.5	.0	−14.3	30	17.1
18	9	Catalyst 9 oxidized with air at 400° and reduced	48.5	51.5	.0	−40.3	79	74.5
19	2	Catalyst 2 heated in O_2 4 hours at 400° and reduced	50.0	50.0	.0	− 4.3[b]	9	..
20	8	Catalyst 8 heated in O_2 1 hour at 500 and reduced	50.0	50.0	.0	− 2.0[b]	4	..

[a] A second run with same charge of catalyst gave almost double this contraction. [b] Contraction of gas volume only took place at beginning of run. [c] By condensation and fractional distillation exit gas contained 81.8% ethane. [d] Exit gas passed through dry-ice trap gave no liquid condensate.

the formation of a fluffy oxide having a tea-leaf appearance, has given products exhibiting erratic catalytic behavior. As indicated in the table, a variation of from 2 to 80% conversion may be obtained with successive preparations. Ignitions carried out in air, nitrogen and hydrogen have proved that the catalytic activity is not greatly influenced by the nature of the atmosphere in which the ignition is conducted. It is instead a function of the heat treatment. It has been possible to duplicate the results shown for Runs 1 and 2 by giving careful attention to the size of the mass undergoing decomposition at any one time. Ignition in deep layers permits a greater mass heat effect which results in lowered activity. A product of good activity is obtained, however, by igniting the bichromate in thin layers, which facilitates rapid dissipation of the heat. Close inspection of the ignited material reveals a non-homogeneity represented by the presence of particles of different color. It is believed that the dark colored part is the only fraction that is catalytically active. The product obtained by ignition in deep layers is much brighter green than that prepared in thin layers. It does not exhibit the glow phenomenon when heated whereas the active material glows feebly when heated to 500°.

When ammonium bichromate is heated in a vacuum at 200–250°, it slowly darkens and gradually evolves water, ammonia and nitrogen. After four or five hours there remains a glistening black residue which contains no ammonia and is slightly paramagnetic. This oxide was found to be stable at temperatures up to 400°. When further heated it suddenly glows, leaving a light green residue. Reaction tests showed that the unglowed sample was moderately active (Run 3) while samples that had been heated above the glow point were without activity (Runs 4 and 5). Ignition of chromium oxalate or nitrate at moderate temperatures yielded catalysts that were inactive for ethylene hydrogenation. This fact is especially interesting in view of the frequency with which both of these methods have been suggested and used for the preparation of active catalysts of other compositions.

The reduction of chromic acid with alcohol followed by precipitation with ammonium hydroxide is a well-known step in the separation of chromium from certain other elements. When this method was applied to the preparation of chromium oxide catalysts, the precipitates formed were different in character from those obtained under similar conditions from trivalent salts. The precipitates from reduced chromates were of a chalky blue-green color and had a powdery texture after washing and drying, whereas the hydrated oxides prepared from the trivalent salts were dark green and dried to glassy gel-like masses. Evidence will be presented later to show that the difference observed is at least partly due to a higher state of oxidation in the case of the reduced chromate catalysts. As indicated by the results of Runs 9 and 10 on the one hand and Runs 12

and 13 on the other, there is little to choose between these two sources of raw material for catalyst preparation. Both yield very active catalysts. Experience has shown, however, that the freshly precipitated gel-like products are less susceptible to the glow phenomenon. Catalysts 12, 13 and 14 prepared by use of alkalies other than ammonium hydroxide had uniformly poorer activities than those prepared with ammonium hydroxide, indicating the detrimental effect of alkali metal compounds as impurities. The reaction between ammonium chromate and a trivalent chromium salt yields a product that contains ammonia, is highly susceptible to the glow phenomenon, and consequently has a low activity for the hydrogenation of ethylene (Run 6).

Precipitation of chromium nitrate with ammonium hydroxide as represented by Catalyst 11 is perhaps the most convenient and reliable method for preparing an active chromium oxide catalyst. This catalyst was used for determining the lower temperature limits of the hydrogenation reaction. Hydrated chromium oxide becomes active at 350–370°. At higher temperatures hydrogenation is rapid, resulting in a temperature rise of about 40° in the catalyst bed. Catalyst 11 was also used for the hydrogenation of propylene and octylene. Under the conditions of Run 13, the conversion of propylene to propane was 43%. In carrying out the hydrogenation of the higher boiling compound, a hydrogen stream containing 2% of normal octylene vapor was passed over the catalyst at the usual space velocity. The iodine number of the recovered condensate indicated a conversion of 95% to saturated products. These results reveal the general applicability of the reaction.

Oxidation and Reduction Reactions of the Catalyst.—In the course of preparing samples for the hydrogenation tests it was early observed that the blue-green chromium hydroxides were reducible. A sample of Catalyst 9 dried at 400° in nitrogen evolved water copiously when the gas was changed to pure hydrogen. This reduction was accompanied by a change in color from the original blue-green to a greenish brown. Careful treatment with air led to a black product which could be reduced again. The reduced oxide was pyrophoric and very active for hydrogenation. On the other hand, if the oxidation was carried out with oxygen at 500°, subsequent reduction yielded a bright green product that was catalytically inactive and apparently no longer susceptible to further oxidation or reduction. The hydrated chromium oxide gels prepared from chromic salts appeared to be unaltered by heating in air or hydrogen.

In order to obtain more accurate data on the reduction reactions observed, the hydrogen consumption of weighed analyzed samples was determined in apparatus designed especially for the study of oxide reductions.[5] At 400° Catalyst 9 (*ex*-sulfate) consumed about 0.75 mole of hydrogen

[5] Taylor and Starkweather, THIS JOURNAL, **52**, 2314 (1930).

per gram atom of chromium whereas only 0.5 mole is theoretically required to reduce CrO_2 to Cr_2O_3. However, the catalyst contained sulfate equivalent to 3.8 weight per cent. of sulfur. That this sulfate was reduced at least in part to sulfide was evidenced by the formation of hydrogen sulfide during the reduction. The hydrogen consumption was in excess of that necessary for complete reduction of the sulfate, which shows that this was not the only reduction taking place. Catalysts 10 and 11 prepared as the hydroxides from chromium chloride and nitrate, respectively, required for reduction only 0.2 mole of hydrogen per gram atom of chromium. The reduction data cannot be interpreted accurately on account of the fact that it was practically impossible to wash the chromium hydroxide samples completely free from salts. In an attempt to determine the initial state of oxidation, several of these samples were evacuated at high temperatures with a Toepler pump and in every case the evolved gases contained, in addition to oxygen, acidic components corresponding to the salts used in preparing the catalysts. The reduction data are sufficiently accurate however to establish the wide difference in oxidation level of the products from the alcohol-reduced compounds and those from commercial trivalent salts.

x-Ray Analysis.—Dr. A. W. Kenney of this Laboratory has obtained Debye–Scherrer diffraction patterns of several catalysts tested for ethylene hydrogenation. Exposures were made on catalysts before and after use and in the glowed and unglowed condition. Catalysts 1, 6 and 7, all of which were prepared by ignition processes and were catalytically inactive, gave the characteristic pattern of a well-defined crystalline chromium sesquioxide.[6] Catalyst 2, which was prepared by a more gentle heat treatment and was found to be active, yielded a diagram indicating dilution of the crystalline oxide with amorphous material. None of the precipitated catalysts, whether prepared from reduced chromic acid or from chromic salts, yielded diffraction patterns when exposed to x-rays, demonstrating the amorphous character of these materials. Catalyst 9 was unchanged in this respect after having been employed for hydrogenation, but Catalyst 11 contained a trace of crystalline oxide after only one hour of use. Glowing of any of the amorphous catalysts resulted in the formation of products having the typical diffraction pattern of chromium sesquioxide. Oxidations and reductions carried out under conditions leading to the formation of the light green reduction product were also found to develop the crystalline state.

Dehydrogenation and Dehydration of Ethanol.—The effect of the glow phenomenon on the catalytic characteristics of chromium oxide is further illustrated by results obtained in a series of experiments on the catalytic decomposition of alcohol. Ethanol vapor was passed over small samples of Catalysts 11 and 11A under the conditions indicated in Table II. Run 2 was made with a sample that had been heated in air to 600° before

[6] Davey, *Phys. Rev.*, [2] **21**, 716 (1923).

use while Runs 3–5 were made consecutively on a sample of a duplicate catalyst. During the interval between Runs 4 and 5, the catalyst was heated in hydrogen to 530°, at which temperature it glowed with an observed rise in temperature of about 100°. The data presented in the table represent the performances of the respective catalysts during the first hour of use.

TABLE II

DECOMPOSITION OF ETHANOL

Run	Catalyst	Catalyst vol., cc.	Alcohol flow, cc./hr.	Temp., °C.	Gas evolution, liters/hr.	Gas composition, H_2	C_2H_4	% C_2H_6
1	No. 11	3	60	375	2.62	42.8	48.6	3.1
2	No. 11 (heated to 600°)	3	62	375	1.51	57.5	35.4	..
3	No. 11A	5	60	415	5.40	40.4	50.6	3.9
4	No. 11A	5	60	430	6.20	42.6	48.7	4.5
5	No. 11A (glowed)	5	55	430	3.38	66.4	29.1	1.8
6	ZnO	3	90	380	6.20	69.3	25.8	0.0

Although the activity of the catalyst is impaired by glowing, it is not destroyed to as great an extent for dehydrogenation as for the hydrogenation of ethylene. This fact is also evident in the last column of the table. The difference in total dehydrogenation and dehydration activity for Runs 4 and 5 as measured by gas evolution is only about 45%, whereas the decrease in saturated hydrocarbon formation is about 78%. Catalyst 11 had an activity for alcohol decomposition equal to 42% of that of zinc oxide (*ex*-oxalate) at 375°, whereas Sabatier's[7] chromium oxide was 70% as active as his zinc oxide. Sabatier also reported a dehydration–dehydrogenation ratio of 10 compared with 1.1 obtained in this work. Both researches[8] are in accord, however, in finding that heat treating the catalyst shifts the ratio in the direction of a greater proportion of dehydrogenation. As in the case of zinc oxide,[9] a shift in the temperature of decomposition of alcohol over chromium oxide has little effect on the ratio of dehydration to dehydrogenation.

Dehydrogenation of Cyclohexane.—The fact that amorphous chromium oxide is capable of catalyzing the hydrogenation of ethylene suggested a test of its activity in the dehydrogenation of hydrocarbons. Cyclohexane was chosen for the experiment because the position of the equilibrium in the temperature range required is favorable while that of the dehydrogenation of ethane is unfavorable. Cyclohexane was passed over 3-cc. samples of Catalyst 11 at the rates of flow indicated in Table III. Glowing was induced in the catalyst used for Run 4 by heating the unglowed oxide to 510°. Several other oxides were employed as controls.

[7] Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 252.

[8] Sabatier and Mailhe, *Ann. chim. phys.*, [8] **20**, 304 (1910).

[9] Adkins and Lazier, THIS JOURNAL, **48**, 1671 (1926).

TABLE III

DEHYDROGENATION OF CYCLOHEXANE

Run	Catalyst	C_6H_{12} flow, cc./hr.	Temp., °C.	Gas evolution, liter/hr.	Benzene in condensate, %
1	Glass wool	60	420–500	0.00	0.08
2	No. 11	57	410	1.50	1.56
3	No. 11	78	430	2.24	3.12
4	No. 11 (glowed)	110	410	0.00	..
5	ZnO	80	410–480	.16	0.33
6	SiO_2 gel	80	410	.00	.0
7	Al_2O_3	80	410	.00	.0

While cyclohexane is apparently stable at temperatures up to 500° in the absence of an active surface, as shown by the results obtained with glass wool, the compound is dehydrogenated by unglowed chromium oxide. Zinc oxide and glowed chromium oxide, on the other hand, are relatively inactive as catalysts for the reaction even at much higher temperatures. Alumina and silica gel are also non-catalysts for the reaction in the temperature range studied.

Other Reactions Catalyzed by Chromium Oxide.—Several chromium oxide catalysts have been tested for the high pressure synthesis of methanol in the course of a comprehensive survey of the subject. The results given in Table IV were obtained with gaseous mixtures containing about 58% hydrogen, 35% carbon monoxide and 1 to 2% each of nitrogen, carbon dioxide and methane. The yields are reported on the basis of a 100-cc. catalyst sample, although a lesser quantity was used in some of the experiments.

TABLE IV

METHANOL SYNTHESIS WITH CHROMIUM OXIDE CATALYSTS

Run	Cat. no.	Catalyst composition	Temp., °C.	Pres., atm.	Space velocity	Yield of crude condensate[a]	Composition of condensate % MeOH	Composition of condensate % Higher alcs.	Yield pure methanol[a]	Yield higher alcs.[a]
1	12	Hydrated	439	290	5,000	27.5	40	..	11.0	...
		Cr_2O_3 Gel	440	290	10,000	36.0	60	..	22.5	...
			450	290	20,000	74.0	70	..	52.0	...
2	6	Cr_2O_3 (*ex*-oxalate)	375	280	10,000	43.0	41	..	17.6	...
			420	280	10,000	36.0	40	..	14.5	...
			450	280	10,000	39.0	34	23	13.2	9.0
3	1	Cr_2O_3	425	280	10,000	14.0	48	7	6.7	1.0
		(*ex*-$(NH_4)_2CrO_4$)	450	280	10,000	19.0	30	17	5.7	3.2
4	5	Chromium chromate	400	272	19,200	22.0	63	14	13.9	3.1
			448	272	19,000	26.0	49	22	12.7	5.7

[a] Yields are expressed as cc. per 100 cc. of catalyst per hour.

In general the activity of chromium oxide catalysts for this reaction is low as compared with certain other single oxides. Zinc oxide, for example, when prepared by igniting the oxalate,[10] gives a yield of 70 cc. of pure methanol per 100 cc. of catalyst per hour when used under the first set of

[10] Lazier, U. S. Patent 1,746,781, Feb. 11, 1930.

conditions of Run 2. Chromium oxide gel is the most efficient chromium oxide catalyst. When removed from the reaction vessel, this catalyst was unchanged in appearance, whereas Catalysts 1, 5 and 6 had assumed the bright green color characteristic of a glowed chromium oxide. Although none of the samples was heated above the temperatures indicated, the poorer showing made by each of the last-named samples is in all probability due to the type of sintering which results in crystallization and in the case of ethylene hydrogenation causes a much larger decrease in catalytic activity.

Like many other oxides, chromium oxide, particularly in the hydrated form, is an active catalyst for the conversion of water gas and steam to hydrogen and carbon dioxide. The reaction takes place at temperatures up to 500° without carbon deposition. The work of Beekley[11] indicates that preservation of the activity of the catalyst is contingent upon prevention of the glow phenomenon, although no indication is given as to whether the sensitivity in this case corresponds with that observed for hydrocarbon hydrogenation or for alcohol synthesis and decomposition.

Observations on the Glow Phenomenon.—The large number of tests incident to the investigation of the catalytic properties of chromium oxide have furnished an excellent opportunity for observing the glow phenomenon as it affects this particular oxide. It has been found that the transformation is not associated with any one source of the oxide or method of preparation but with all amorphous catalysts. The phenomenon is not dependent on a gel structure as ordinarily manifested by the outward appearance of a precipitate, since the powdery chromium oxides obtained from reduced chromates glow even more readily than those of a gel-like character. Amorphous chromium oxide glows when strongly heated regardless of the nature of the atmosphere which happens to surround it. If the nature of the gas affects the temperature of glowing, as is sometimes the case, it is because a reaction such as reduction of a higher oxide or oxidation of adsorbed hydrogen is initiated on the surface which produces heat effects that accelerate what would otherwise be a spontaneous transformation. No specific state of oxidation appears to be necessary since glowing has been experienced with both oxidized and reduced samples. The glow may take place without evolution or adsorption of gases but water is copiously evolved. In case the unglowed oxide is in a higher state of oxidation than Cr_2O_3, oxygen is eliminated in the process, leaving a residue of Cr_2O_3.

Discussion

The outstanding fact uncovered by the experimental work is that chromium oxide is inherently capable of bringing about the hydrogenation of the alkene bond, a distinction which sets it apart from all of the other hydrogenating–dehydrogenating oxides so far studied. On account of the several

[11] Beekley, U. S. Patent 1,789,538, Jan. 20, 1931.

methods used for the production of active catalysts and the precautions taken in the purification of the starting materials, it is not reasonable to attribute the results obtained to the presence of an impurity. Assuming that in order to obtain hydrogenation, activation of both hydrogen and the compound to be hydrogenated is necessary, it is apparent that chromium oxide differs from the other oxides in that it is *capable of activating hydrocarbons*, for many oxides are capable of catalyzing the hydrogenation of carbonyl groups in processes which must also require hydrogen activation. A practical application of this concept is found in the reported use of chromium oxide as a major component of catalysts for the destructive hydrogenation of coal and petroleum,[12] and it is possible that such a catalyst might also be useful for other reactions of the unsaturated hydrocarbons.

Equilibrium considerations and the necessity of avoiding the glow phenomenon have precluded an attempt to investigate the reverse reaction of dehydrogenation of simple saturated hydrocarbons. It can be assumed, however, that the cyclic hydrocarbons should behave in a manner analogous to the alicyclic series; in fact, the same differences between zinc and chromium oxides observed in ethylene hydrogenation were found to hold for the dehydrogenation of cyclohexane. The same forces are apparently at play in these two cases. This is another instance in support of the proposal that the mechanism of hydrogenation and dehydrogenation is the same.

Another important point established by the experimental work is the discovery that the capacity of chromium oxide for hydrogenation and dehydrogenation of hydrocarbons is linked to the amorphous form alone. x-Ray data are readily applicable to the detection of crystalline material, but they cannot be applied with equal facility to the detection of amorphous compounds when crystalline material is also present. In spite of this limitation of the experimental method, it has been shown that any treatment leading to glowing and the consequent development of crystalline material in the oxide resulted in a serious and usually total loss of activity toward hydrocarbons. The same factors however caused relatively minor effects on the activity toward oxygenated compounds as illustrated by the results on methanol synthesis and dehydrogenation of ethanol. The amorphous state is not in general a prerequisite for catalytic activity since the hydrogenating oxides previously studied were all crystalline in character.

The high-temperature loss of capacity for hydrocarbon activation appears to contribute to a further understanding of the mechanism of the glow phenomenon. Weiser[13] believes that "there is little doubt but that the glow is due to a very sudden decrease in the large surface of the oxides

[12] See especially British Patent 251,264 filed April 14, 1926, and 311,251 filed December 5, 1927.

[13] Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926, p. 79.

prepared by precipitation" while Böhm[14] and Blanc[15] have reached the conclusion as a result of x-ray studies and thermal analyses that the transformation is only a change from the amorphous to crystalline state. Measurement of catalytic activity should provide a sensitive test for any substantial decrease in surface. The effect of the glow phenomenon on activity toward hydrocarbon activation, if taken alone, would be exactly what to expect if Weiser's explanation is the correct one. Our x-ray findings confirm those of Böhm, and the results on alcohol decomposition and methanol synthesis indicate no greater loss of active surface than may be readily obtained by mildly sintering a crystalline oxide catalyst. While it is believed that the catalytic observations reported have a significant bearing on the mechanism of the glow phenomenon, it is inadvisable in the present state of our knowledge to attempt a more elaborate interpretation of the results obtained.

The preparation of an oxide capable of glowing by partial ignition of ammonium bichromate throws some light on the mechanism of the decomposition of this salt. It is of interest to note that the heat evolved is due only in part to the oxidation of ammonia. The remainder is furnished by the glow phenomenon. It is evident that the arrangement of oxygen and chromium atoms in ammonium chromates is as unstable as in the precipitated trivalent oxides. Mellor[16] states that chromium oxide prepared by igniting ammonium bichromate is amorphous. In view of our experimental results, this statement holds good only for the oxide prepared at low temperatures in a vacuum.

The theoretical treatment of contact reactions is usually based on the concept of a crystalline catalyst in which the surface presents a definite pattern which is held responsible for the direction of the reaction. In an extension of these ideas the authors[17] explained the non-activity of oxides for hydrogenation of alkenes by assuming that the residual valences of the metal atoms of the surface which ordinarily function as hydrogenation centers were dissipated in metallic oxides by the surrounding oxygen atoms. The present case of amorphous chromium oxide cannot be treated in the same way, since as far as we know there is no regular arrangement of atoms in the surface of amorphous materials.

The dehydrogenation of cyclohexane over *amorphous* chromium oxide constitutes a formidable obstacle to Balandin's theory[18] requiring a surface lattice of a certain configuration. The theory further requires that before catalysis can occur the permissible spacing of the atoms must be within

[14] Böhm, *Z. anorg. allgem. chem.*, **149**, 217 (1925).

[15] Louis Blanc, *Ann. chim.*, [10] **6**, 182 (1926).

[16] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1931, Vol. XI, p. 177.

[17] Vaughen and Lazier, THIS JOURNAL, **53**, 3719 (1931).

[18] Balandin, *Z. physik. Chem.*, **B2**, 289 (1929).

narrow limits the symmetry of the active points of the catalyst coinciding with the symmetry of the adsorbate. Unlike the hydrated chromium oxide catalyst, zinc oxide is crystalline, and the arrangement of the zinc atoms is similar to that of metallic zinc, but the spacings between zinc atoms in the oxide are wider than in the case of the metal. In zinc oxide the interatomic distance is about 3.25 Å. as compared with 2.8 set by Balandin as the upper limit for an active hydrogenation catalyst.

A discussion of the relationship of the physical, chemical and catalytic properties of chromium oxide should not be concluded without reference to the possible role played by water. Most of the active preparations studied were highly hydrated, the water being so tightly held that it was not removed in appreciable quantities at the relatively high temperatures of the catalytic tests. The catalyst prepared by the controlled ignition of ammonium bichromate was no exception, since this oxide was found to retain a portion of the water formed by the oxidation of ammonia during ignition. On the other hand, the glow phenomenon results in an effective and probably non-reversible expulsion of water which must of itself alter the chemical nature of the surface. The changes in catalytic properties of chromium oxide resulting from the glow phenomenon cannot be definitely associated either with the chemical changes caused by dehydration or the physical changes manifested by x-ray analysis.

Experimental Part

Catalyst Preparation.—On account of the large number of catalysts prepared and tested it will be impossible to give the complete details of preparation of each. In presenting this section care has been taken to set forth only such information as, in the present state of our information, is regarded necessary to obtain reproducible results. Catalysts 1 and 2 were prepared by igniting C. P. ammonium bichromate. The salt was freed from traces of iron by dissolving in strong ammonia solution, allowing to stand at 40–50° and removing the iron hydroxide sludge by filtration. For Catalyst 1, 100 g. of the dry salt was placed in a 650-cc. loosely covered casserole and heated in a muffle furnace at 400° for thirty minutes, no effort being made to control the rate of decomposition or temperature of the mass. In preparing Catalyst 2, 1-g. portions of the salt were warmed over a flame until ignition was initiated. Catalysts 3 and 4 were prepared by slowly heating 15-g. samples of ammonium bichromate in an oil-bath under the vacuum produced by a Cenco Hyvac pump. In the first case decomposition was observed to set in at about 200° and the sample was not heated above 245°. For the second preparation, the temperature was raised to 500° after four hours of heating at the lower temperature. A second change in the character of the product was evident at about 485°. In the preparation of Catalysts 5 and 6 chromium nitrate and oxalate, respectively, were heated for four hours in a muffle furnace controlled at 400°. The following procedure was employed for the preparation of Catalysts 8 and 9. A hot solution containing 150 g. of ammonium bichromate dissolved in 500 cc. of water was poured slowly into a boiling solution of 200 cc. of sulfuric acid (or such a volume of concentrated hydrochloric acid as is equivalent to the sulfuric acid indicated) and 150 cc. of methanol in 500 cc. of water. The reduction product was diluted with 5 volumes of water, cooled to room temperature and precipitated by the addition of a slight excess of ammonium hydroxide.

Catalysts 10–14 inclusive were prepared by the addition at room temperature of the appropriate alkali precipitating agents to 0.04 molar solutions of C. P. trivalent chromium salts. All precipitated catalysts were washed five to ten times by decantation with a volume of water at least equal to the mother liquor. In one case a dialyzed sample was found to give the same catalytic results as an undialyzed sample. Catalyst 5 was prepared by adding an equivalent of ammonium chromate to chromium nitrate, the other conditions being the same as for the precipitated hydroxides. All of the precipitated catalysts were dried at 110°, and suitable physical form was obtained by breaking up the filter cake and collecting the 8–14 mesh material. These products were subject to a 20% shrinkage when heated in place in the reaction apparatus but no allowance was made for this in measuring the catalyst charges. Catalysts prepared by ignition processes were granulated by briquetting. The samples of zinc oxide and alumina used for reference catalysts were prepared by ignition of zinc oxalate and aluminum hydroxide, respectively.

Apparatus and Experimental Method.—The apparatus used for the hydrogenation of alkenes was the same as that described for this purpose in the earlier paper.[19] In every case the catalyst sample was heated to the reaction temperature in a slow stream of hydrogen. All oxidations or reductions on samples to be tested for this reaction were made in place by by-passing the gasometers. The furnace temperature was controlled by a Republic pyrometer while the temperature of the interior of the catalyst bed was simultaneously recorded by a Leeds and Northrup controller-recorder.

Gas analyses were made on a Fisher Universal Gas-Analyzing Apparatus. The necessity of burning only a small aliquot of samples containing a high ethane content often led to somewhat discordant results, necessitating repeated analyses. In view of Lenher's discovery[20] that a trace of oxygen is able to initiate a polymerization of ethylene to higher alkenes, it was desirable to determine whether any saturated hydrocarbon other than ethane was formed. In two representative experiments on the hydrogenation of ethylene, analyses of the effluent gases were made by Dr. D. F. Babcock in the Podbielniak fractional-distillation apparatus.[21] These data were in very good agreement with those obtained by the combustion method and proved conclusively the absence of saturated hydrocarbons other than ethane. In the preparation of Table I, the ethylene conversions were calculated from the inlet gas compositions and contractions observed on passage over the catalysts. The analyses for ethane served to confirm the conclusions reached in this way. In some cases, particularly in connection with the dehydrogenation experiments, the gas analyses reported do not equal 100% for the reason that negligible amounts of nitrogen, carbon dioxide or carbon monoxide initially present in the apparatus or formed as side reactions are not included in the tabulated data.

The experiments reported on the dehydrogenation of ethanol and cyclohexane were carried out in apparatus patterned after that of Adkins and Nissen.[22] The accuracy, efficiency and convenience of this apparatus have been improved by so many alterations and additions over a period of six years' use in this Laboratory that it is thought worth while to describe the improved set-up in some detail. The added features are (1) automatic regulation of the mercury head of the feed device, (2) provision for refilling without disassembling, (3) semi-automatic control of the gasometer pressure and volume and (4) provision for gas sampling at constant pressure and without interrupting the progress of the experiment. By mounting the reaction tube and furnace in a vertical position, channeling of the catalyst bed due to shrinkage is prevented. With a 46-cm. reaction

[19] Vaughen and Lazier, THIS JOURNAL, **53**, 3719 (1931).

[20] Lenher, *ibid.*, **53**, 3752 (1931).

[21] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

[22] Adkins and Nissen, THIS JOURNAL, **46**, 140 (1924).

furnace a separate preheating furnace may be omitted, the indentations in the upper part of the reaction tube furnishing an adequate heating surface.

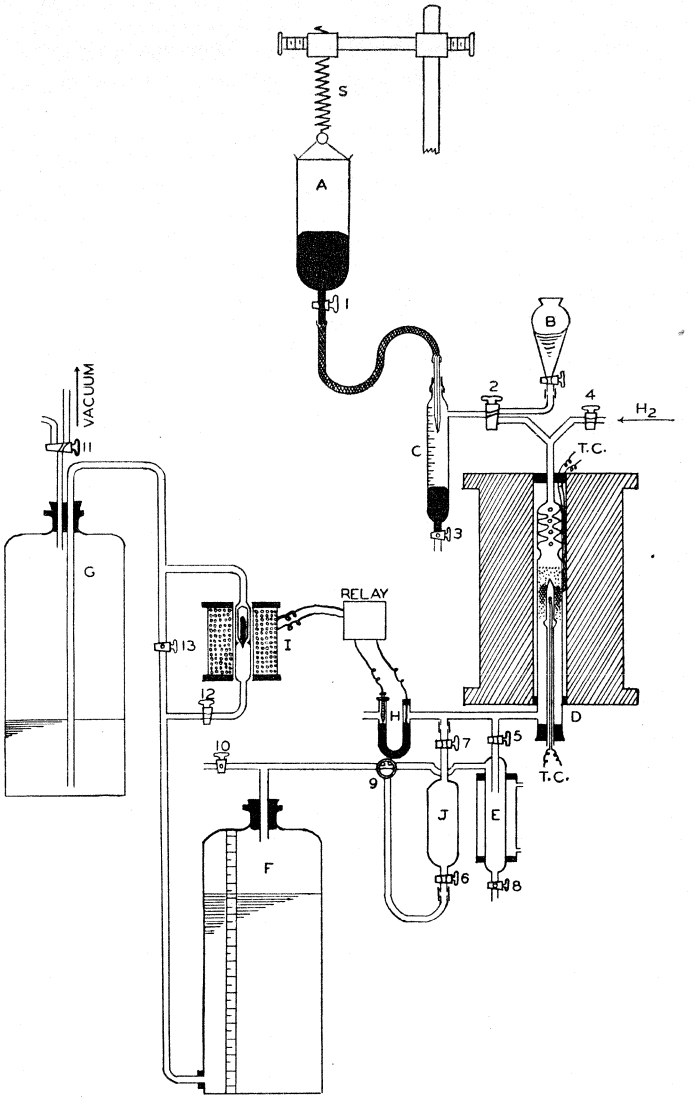


Fig. 1.—Dehydrogenation apparatus.

The liquid to be treated is stored in the flask B, from which it is drawn to fill the buret C. From here it is displaced into the reaction tube D with mercury, which enters the buret at a constant rate through a capillary. Refilling is accomplished by turning Stopcock 2 and draining out the mercury at 3. The characteristics of the springs and the diameter of the mercury reservoir A are so chosen as to maintain a constant head of mercury on the capillary.

A Y-tube is provided at the head of the reaction vessel to permit the passage of hydrogen over the catalyst during its pretreatment. The catalyst is held in place in the reaction tube with plugs of glass wool, the lower plug being supported by a button on the thermocouple well, through which a thermocouple reaches the interior of the catalyst bed. Another thermocouple is placed at the catalyst level against the outside of the tube. Temperature control and records are obtained as outlined for the ethylene hydrogenation apparatus.

The liquid products are condensed in the water-cooled trap E, and the gaseous products pass into the gasometer F. Water is drawn out of the gasometer by suction on bottle G, and the rate of withdrawal is controlled by the manometer H and solenoid valve I. The collecting system used in this work was capable of receiving a gas evolution of about 20–25 liters per hour, with a deviation from atmospheric pressure of only a few millimeters. At definite intervals the exit gas was sampled by turning stopcock 9, which permitted gas to displace the water in sample bottle J into the gasometer F. Saturated salt solution was used as the retaining liquid, and a little of it was left in the sample bottle when sampling in order to displace dissolved gases from the condensed alcohol. Small quantities of benzene in cyclohexane were determined by use of the refractometer.

The apparatus assembly used for methanol synthesis was essentially the same as that described by Lewis and Frolich.[23] The average duration of operation at each set of conditions was four hours, the same charge of catalyst being used at a number of different temperatures.

Materials.—Ethylene and hydrogen of 98–99% purity were procured from commercial storage cylinders. Propylene was prepared by the catalytic dehydration of isopropanol over an alumina catalyst. Absolute ethanol was used for the dehydrogenation tests. The cyclohexane and octylene were Eastman Nos. 702 and 1821. The synthetic water gas used for methanol synthesis was prepared by mixing cylinder hydrogen with carbon monoxide prepared by blowing carbon dioxide over heated coke.

In addition to references already made, the authors also acknowledge the assistance and helpful criticism of Drs. G. B. Taylor and H. G. Tanner of the Experimental Station staff.

Summary

Amorphous chromium oxide has been found to be an active catalyst for the hydrogenation of ethylene, propylene and octylene and for the dehydrogenation of cyclohexane, differing in this respect from any other hydrogenating oxide tested. Experiments on a variety of catalyst preparations bear out the conclusion that this behavior is not associated with any particular impurity, source of materials or method of preparation but is inherently associated with the amorphous state of chromium oxide. Any treatment leading to glowing with consequent development of crystalline material in the oxide greatly impairs or destroys activity for the hydrocarbon reactions. Activity for methanol synthesis or dehydrogenation of ethanol is less affected by such treatment.

Chromium oxide is quite active for alcohol decomposition, giving about 50% each of dehydration and dehydrogenation. Heat treatment causes a shift in the ratio in the direction of a greater proportion of dehydrogenation.

[23] Lewis and Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928).

A number of observations on the glow phenomenon have been recorded, the most interesting and important fact uncovered being that the glow phenomenon, which invariably results in the crystallization of the chromium oxide, also results in the loss of capacity of the catalyst for activating hydrocarbons. The bearing of these experimental results on current theories of catalysis is discussed.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE THEORY OF THE GLASS ELECTRODE. II. THE GLASS AS A WATER ELECTRODE

BY MALCOLM DOLE

RECEIVED MARCH 14, 1932 PUBLISHED AUGUST 5, 1932

Introduction

The inability of the glass electrode to function as a perfect hydrogen electrode in alkaline solutions has recently been explained[1] on the assumption that sodium or other positive ions as well as hydrogen ions may have an appreciable mobility across the aqueous solution glass boundary. This theory, however, fails to account for the interesting errors of the glass electrode in very acid solutions recently discovered by MacInnes and Belcher and by Buchböck[2] inasmuch as the current carried by the sodium ion across the boundary becomes less and less as the hydrogen-ion concentration increases and the hydrogen ion carries more and more current. Since

[1] Dole, THIS JOURNAL, **53**, 4260 (1931). The author wishes to publish the following corrections to this paper. On page 4271 a statement was made concerning the work of Lengyel which is, perhaps, a bit misleading in that Lengyel's experimental procedure was not fully described. Lengyel considered his quartz membranes as condensers, but since he used his electrometer as a null point instrument, the relative capacity of the quartz membrane and of the condenser did not matter; it is only on attempting to measure the potential difference directly by the electrometer deflections that the capacity of the electrometer must be considered in relation to the capacity of the quartz membrane.

The author also wishes to emphasize further concerning his theory of the glass electrode that the experimental equation is highly empirical in that the slope and intercept have to be found from the data; they cannot be calculated. The theoretical significance of the equation rests in the analogy between the empirical equation and one derived on the basis of liquid junction theory (after making several hypothetical assumptions). Hence in reading the author's second paper on the theory of the glass electrode this should be borne in mind.

A misunderstanding has arisen over the mention of the name of Dr. MacInnes in reference 1 of the author's first paper. Dr. MacInnes does not subscribe to the author's theory as given in this paper; Dr. MacInnes' own theory of the glass electrode appeared in a paper previously published with Belcher, THIS JOURNAL, **53**, 3315 (1931).

[2] Buchböck, *Z. physik. Chem.*, [A] **156**, 232–236 (1931); MacInnes and Belcher, THIS JOURNAL, **53**, 3315 (1931).

the migration of the sodium ion becomes negligible at a hydrogen-ion concentration of 1×10^{-8}, it can be readily seen that a different explanation is necessary for the acid solution errors. There have been certain theories proposed to account for these results, but they have not proved to be entirely satisfactory. Hence this investigation was undertaken in order to obtain more experimental data and to obtain an explanation for the behavior of the glass electrode in acid solutions which will be thermodynamically sound and which will agree quantitatively with the data.

Experimental

The apparatus and experimental technique were identical with that already described.[1,3] The glass electrode was carefully compared with the hydrogen electrode in pure solutions of hydrochloric acid and sulfuric acid. A comparison at approximately constant chloride-ion activity was carried out by adding 2 *N* hydrochloric acid to 4.4 *N* lithium chloride. Experiments were performed to find out if varying the positive ion affected the errors; *e. g.*, sodium sulfate, aluminum sulfate, lithium chloride, sodium chloride and aluminum chloride solutions were used in the comparison. These experiments likewise enabled a comparison to be made of the relative effect of the chloride and sulfate ions in causing the acid solution errors. Finally some experiments in ethanol solutions were performed to test any possible effect due to a change in the concentration of the solvent water. These experiments were carried out by adding absolute ethyl alcohol to an aqueous solution of hydrochloric acid at a P_H of about one and comparing the glass electrode with the hydrogen electrode as the concentration of the water was changed. The comparison in the approximately 98% ethanol was performed in a separate experiment. A comparison of the glass and hydrogen electrodes was also made in an ethanol solution of sodium iodide over a considerable P_H range by adding aqueous sodium hydroxide to the solution.[4]

All the P_H values of the tables were calculated neglecting the liquid junction potential between the saturated potassium chloride solution of the salt bridge and the solution under investigation. The data which are

[3] Since the first paper was submitted for publication, a paper by MacInnes and Belcher has appeared[2] in which it is stated that the potentials of the glass electrode in alkaline solution are not reproducible and that different potentials are obtained depending on the direction of the titration, *e. g.*, whether the P_H is changed by adding base to acid or acid to base. These results are contrary to those found by the author, who obtained reproducible results in sodium and lithium alkaline solutions and who obtained the same results irrespective of the manner in which the P_H was changed. The anomalous results of MacInnes and Belcher may be attributed to the fact that in their titrations the sodium-ion concentration was not held constant, as it was in the author's experiments. On adding sodium hydroxide to hydrochloric or acetic acid, the sodium-ion concentration is continually increasing and is indefinite, and on adding the acid to the base the sodium-ion concentration would decrease continually; hence one would expect to get different results depending on the direction of P_H change when the experiments are carried out in this way, since in alkaline solutions the potentials are functions of the sodium-ion concentration.

[4] The hydrogen–platinum electrodes apparently behaved reversibly in sodium iodide–ethanol solutions although in the neighborhood of the neutralization point they drifted slowly in the direction of higher P_H values. No reproducible results were obtained in barium iodide–ethanol solutions; hence these results are not given.

collected in Tables I to IV are not as reliable as the errors in alkaline solutions for they were not so reproducible nor so reversible. A study of the

TABLE I

ERRORS OF THE GLASS ELECTRODE IN HYDROCHLORIC ACID SOLUTIONS AT 25° IN MILLIVOLTS

HCl solutions

Glass electrode no. P_H	−0.272	−0.458	−0.543	−0.680	−0.730	−1.67
C-97	−1.1		−2.8		−15.1	
F-17		−1.1				
G-11				−6.5		−18.4
G-14				−6.8		

2 *N* NaCl + 2 *N* HCl

P_H	1.11	0.884	0.590	0	−0.017	−0.240	−0.621
C-92	−0.4		−0.9		−3.0	−7.4	
C-93	− .4		− .7		−2.1	−5.1	
C-97		−5.6		−6.9			
E-1		−2.1		−2.2			−5.7

$AlCl_3$ + Concn. HCl

P_H	2.624	1.119	0.069	−0.646
F-44	0	0	−1.1	
F-48				−8.9

4.4 *N* LiCl + 2 *N* HCl

P_H	C-94	C-97	P_H	C-97	C-98	P_H	D-40	E-7
4.62	− 4.6	− 6.3	4.60	−5.1	−5.1	4.34	−4.1	−6.7
3.46	− 4.0	− 8.1	3.47	−7.4	−6.5	1.94	−4.4	−7.4
1.93	− 5.1	−10.9	1.31	−9.3	−8.7	0.987	−4.4	−6.9
1.09	− 7.3	−11.7	0.795	−7.6	−7.4	.201	−5.7	−6.9
0.57	− 8.2	− 9.4	.308	−7.2	−6.9	− .458	−8.6	−7.3
.047	−12.0	− 7.4	2.68	−7.2	−7.5			
− .477	−18.7	− 7.0						
− .345	−20.8	− 7.3						
+ .144	−16.9	− 7.3						
1.22	− 9.8	− 6.6						
3.44	− 6.4	− 6.3						

TABLE II

ERRORS OF THE GLASS ELECTRODE IN SULFURIC ACID SOLUTIONS AT 25° IN MILLIVOLTS

H_2SO_4 solutions

P_H	−0.798	−0.910	−1.354	−1.620
C-92		−7.8	−16.6	
G-10	3.3			36.3
G-13	6.9			33.9

1 *N* Na_2SO_4 + Concn. H_2SO_4

P_H	−0.512	−0.666
F-51	−0.3	−6.1
F-53	− .7	−5.4

1 *N* $Al_2(SO_4)_3$ + Concn. H_2SO_4

P_H	0.896	0.210	−0.834
F-17	0	−1.7	−8.5
F-21	0	−1.7	−5.1

TABLE III

ERRORS OF THE GLASS ELECTRODE IN ETHANOL SOLUTIONS AT 25° (MILLIVOLTS)

% C_2H_5OH by volume	P_H	Glass electrode no.	Error
33	1.30	F-24	− 1.3
33	0.413	F-35	− 1.3
37	1.86	F-24	− 2.0
55	1.36	F-24	− 4.2
56	1.99	F-24	− 4.6
66	0.712	F-35	− 3.9
98	− .065	F-38	−55.1
98	− .065	F-45	−38.6

TABLE IV

ERRORS OF THE GLASS ELECTRODE IN ETHANOL SOLUTIONS OF SODIUM IODIDE (1 *N*) AT 25° (MILLIVOLTS)

P_H	Glass electrode no.	Error	P_H	Glass electrode no.	Error
4.72	F-38	−31.2	7.73	F-45	+2.2
4.72	F-45	−27.2	8.09	F-38	+6.8
6.79	F-38	−18.6	8.09	F-44	1.5
6.79	F-45	−16.2	12.58	F-38	233
6.88	F-38	−12.2	12.58	F-45	226
6.88	F-44	−16.0	12.75	F-38	232
7.21	F-38	−13.0	12.75	F-44	120
7.21	F-45	−12.7	13.16	F-38	255
7.45	F-38	− 4.8	13.16	F-44	244
7.45	F-44	− 8.5	14.09	F-38	296
7.73	F-38	+ 1.7	14.09	F-44	286

data for the 4.4 *N* lithium chloride solution indicates this fact. The errors are plotted against the P_H in Figs. 1 and 3 and against the concentration of the alcohol in Fig. 2.

Interpretation of the Results

A possible explanation of the errors of the glass electrode in acid solution may be based on the assumption that negative ions are carrying the current across the glass aqueous solution boundary instead of the positive ions. It will be remembered that the errors of the glass electrode in alkaline solutions depended to a large extent upon the particular positive ions present and not at all upon the negative ions. Since the errors of the glass electrode in acid solutions are of opposite sign to those in the alkaline solutions, it might reasonably be assumed that the acid solution errors are due to the negative ions since these ions are charged oppositely to the positive ions. It would be very difficult to see why positive ions could cause any errors in acid solutions; hence if these errors are to be due to ions, they must be due to negative ions. If this were true, the errors in acid solution should be a function of the concentration and nature of negative ions present just as the alkaline solution errors are functions of the con-

centration and nature of the positive ions. A glance at the data, however, indicates that this is not the case. The difference between the chlorides and sulfates is slight in contrast to the large difference, for example, between the sodium and barium errors in alkaline solutions. Furthermore, a large increase in chloride-ion concentration causes no appreciable increase in the error as the results for 4.4 *N* lithium chloride solutions prove. It is also interesting to note that the presence of the triply charged aluminum ion has no effect upon the errors, which indicates that the errors are not caused by any adsorption phenomenon. Because of all of these facts we must reject the hypothesis that the acid solution errors are caused by negative ions. Another possible explanation of the errors is that recently advanced by MacInnes and Belcher.[2] These authors have modified the Horovitzian ionic exchange theory[1] by stipulating that in acid solutions sodium ions in the glass are replaced by hydrogen ions of the solution, thereby diminishing the concentration difference of hydrogen ions between the glass and the outside solution and accordingly the potential. However, by increasing the hydrogen-ion concentration of the glass the potential difference between the glass and the *inside* solution will be increased and it is easy to show mathematically that the resulting increase will just balance the decrease in potential between the glass and the *outside* solution, and no error will result. In other words, as long as the current through the glass membrane is carried solely by hydrogen ions it does not matter at all what the hydrogen-ion concentration in the glass is. An additional theoretical objection to the theory of MacInnes and Belcher is that ionic exchange should occur at all but one P_H since there can only be one concentration of hydrogen ions for a given solution where the free energy of transfer of hydrogen ions will just balance the free energy of transfer of sodium ions (the criterion of zero exchange).[5] A practical objec-

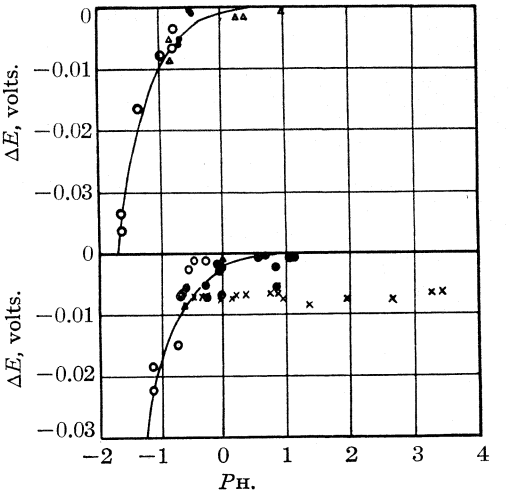


Fig. 1.—Errors of the glass electrode in acid solutions. Top curve: sulfate solutions; circles, H_2SO_4; triangles, $Al_2(SO_4)_3 + H_2SO_4$; solid circles, $Na_2SO_4 + H_2SO_4$. Bottom curve: chloride solutions; circles, HCl; triangles, $AlCl_3$ + HCl; solid circles, NaCl + HCl; crosses, LiCl + HCl; note the constant error in the lithium solutions as the P_H is changed.

[5] In a rapid titration complete thermodynamic equilibrium will never be set up unless the concentration of the aqueous solution happens to be at the concentration which

tion to the ionic exchange theory is that the glass electrode error remains constant at −7.0 millivolts in the 4.4 *N* lithium chloride solution over the large P_H range +4 to −0.5. Neither of the above theories gives any clue to the explanation of this interesting fact. Nor do they explain why the glass electrode fails to function properly in alcohol solutions.

Since neither the concentration nor the nature of the negative or positive ions had any appreciable influence upon the errors of the glass electrode in acid solutions and since the errors also were not a direct function of the hydrogen-ion concentration, it occurred to the author that possibly the change in activity of the water was causing the error. This idea was strengthened further by a study of the alcohol solutions. Such an error could be caused by a transfer of water molecules through the glass by the hydrogen ions as they migrated from one solution to the other. A platinum hydrogen electrode transports, of course, no water when it transfers hydrogen ions from one solution to another; hence if water is transferred through an activity difference by the glass electrode, it is obvious that an additional potential will be introduced which will cause the glass electrode potentials to deviate from those given by a perfect hydrogen electrode. This may be easily demonstrated mathematically provided the assumption is made that as the activity of the water is decreased the number of water molecules carried through the glass per hydrogen ion remains unchanged. If *S* is the number of moles of water carried across the boundary by one equivalent of hydrogen ions, a_{H_2O} the activity of the water (taken as unity in the reference solution inside the glass electrode), a_H the activity of the hydrogen ion, then the equation for the net potential across the glass membrane is[6]

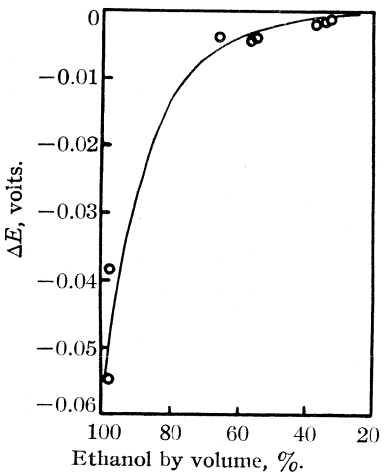


Fig. 2.—Errors of the glass electrode in ethanol–water mixtures.

$$E_1 = \frac{RT}{F} \ln \frac{a'_H}{a''_H} + S \frac{RT}{F} \ln a'_{H_2O} \qquad (1)$$

it would have if equilibrium were allowed to take place. With the concentration of the glass at an approximately fixed value, it is obvious that there can be only one concentration of the aqueous solution that will agree with the equilibrium condition. Hence ionic exchange should occur at all but one P_H according to the theory of MacInnes and Belcher. But the glass electrode agrees with the hydrogen electrode over a billion-fold change of hydrogen-ion concentration without any apparent error.

[6] See Taylor, *J. Phys. Chem.*, **31**, 1480 (1927).

If the glass electrode acted as a perfect hydrogen electrode, the equation would be

$$E_2 = \frac{RT}{F} \ln \frac{a'_H}{a''_H} \qquad (2)$$

Subtracting E_2 from E_1 an equation for the error of the glass electrode in acid solutions is obtained, namely

$$\Delta E = E_1 - E_2 = S \frac{RT}{F} \ln a'_{H_2O} \qquad (3)$$

This equation agrees qualitatively with all the facts observed; it shows that the error is independent of the nature and concentration of any ions present including the hydrogen ion and that the error depends only upon the activity difference of the water between the two solutions. If the activity of the water is diminished, the error will be negative in sign as is actually observed. But it is possible to test equation (3) quantitatively. From data given in the "International Critical Tables" and elsewhere the vapor pressure of the water and therefore the activity in the solutions of hydrochloric and sulfuric acids in the alcohol solutions (assuming that the vapor pressure of the water in the alcohol water mixtures is the same as in the acid mixture actually used), and in the 4.4 N lithium chloride solution may readily be determined.[7] If the activity of the water in the reference solution inside the glass be taken as unity, and if a'_{H_2O} is the activity of the water in the solution under investigation, then by plotting $-\log a'_{H_2O}$ against the error of the glass electrode a straight line should be obtained with slope equal to 0.059 S and with intercept on the abscissa equal to zero if equation (3) is valid. The data necessary for such a graph are collected in Table V, and are plotted in Fig. 4.

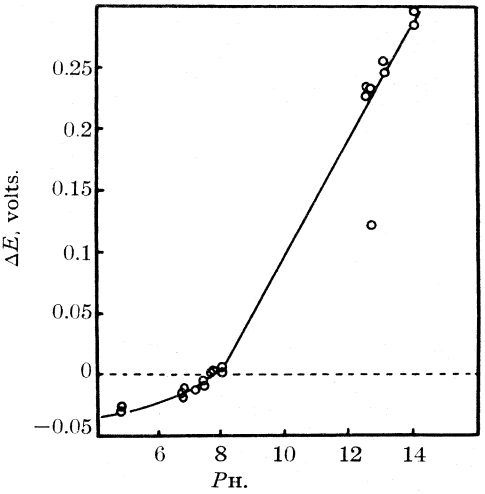


Fig. 3.—Errors of the glass electrode in 1 N sodium iodide in ethanol.

From a study of the data and the graph it is evident that the potentials of the glass electrode agree within the rather large experimental error with the supposition that as the hydrogen ion migrates through the glass it

[7] The solutions of hydrochloric and sulfuric acids were titrated volumetrically in order to find their normal concentrations at the three lowest P_H values.

TABLE V

THE ERROR OF THE GLASS ELECTRODE IN MILLIVOLTS AS A FUNCTION OF THE ACTIVITY OF THE WATER AT 25°

Solution	P_H	a_{H_2O}	ΔE obs.	ΔE calcd. 0.05915 log a_{H_2O}	Diff.
33% ethanol	1.30	0.89	− 1.3	− 3.0	1.7
33% ethanol	0.413	.89	− 1.3	− 3.0	1.7
37% ethanol	1.86	.88	− 2.0	− 3.3	1.3
55% ethanol	1.36	.83	− 4.2	− 4.8	0.6
56% ethanol	1.99	.83	− 4.6	− 4.8	.2
66% ethanol	0.712	.79	− 3.9	− 6.1	2.2
4.4 *N* LiCl	4 to −0.5	.77	− 7.0	− 6.7	−0.3
H_2SO_4	−0.798	.69	− 6.9	− 9.5	2.6
H_2SO_4	− .798	.69	− 3.3	− 9.5	6.2
HCl	− .680	.65	− 6.5	−11.1	4.6
HCl	− .680	.65	− 6.8	−11.1	4.3
H_2SO_4	− .910	.63	− 7.8	−11.9	4.1
HCl	− .730	.62	−15.1	−12.3	−2.8
HCl	−1.17	.41	−18.4	−22.7	4.3
HCl	−1.17	.41	−22.5	−22.7	0.2
H_2SO_4	−1.35	.40	−16.6	−23.5	6.9
H_2SO_4	−1.62	.27	−33.9	−33.6	−0.3
H_2SO_4	−1.62	.27	−36.3	−33.6	−2.7
98% ethanol	−0.065	.12	−55.1	−54.5	−0.6
98% ethanol	− .065	.12	−38.6	−54.5	15.9

carries just one molecule of water along with it (the slope of the line turns out to be equal to 0.059 and S equal to one). The agreement is best for the 4.4 *N* lithium chloride solution; this is perhaps because the error in this solution was the most carefully determined error. In the alcohol, hydrochloric acid and sulfuric acid solutions there is the possibility that alcohol or acid molecules might be transported through the glass; this would cause the error to be lower than theoretically calculated. The agreement between the data and the theoretically calculated values, however, indicates that it is water that is carried through the glass in preference to any other neutral molecule. At constant P_H, therefore, the glass electrode would function as a true water electrode. As far as the author is aware this is the only known example of such an interesting phenomenon.

The errors of the glass electrode in alkaline ethanol solutions of sodium iodide are what might be expected from the behavior of the glass electrode in water. An orienting experiment carried out in a solution of barium iodide indicated that quite analogously with aqueous solutions the barium ion causes considerably less error than does the sodium ion in ethanol solutions. The magnitude of the errors, however, is greater than the errors in water, and due to the complex situation, the errors are rather unexplainable on a quantitative basis.

Conclusions

It is now possible to obtain a complete equation for the glass electrode over practically the entire P_H range by combining equation 3 with equation 15 of the author's previous[1] paper, and including in the final equation the usual equation for the hydrogen electrode. The equation is

$$E = \frac{RT}{F} \ln \frac{a'_H}{a''_H} + \frac{RT}{F} \ln \frac{B/a_H^{(n-1)'} + a'_H}{a'_H} + \frac{RT}{F} \ln a'_{H_2O} \qquad (4)$$

In equation (4) B and n are constants to be chosen from the data; equation 4 also contains the implication that the reference solution inside the glass electrode will not cause any deviation from the correct hydrogen electrode function on the inside surface of the glass electrode.

The question now arises, can a glass electrode be used to measure the hydrogen-ion activity in non-aqueous solvents? The answer is that it surely will not give the correct potentials if the reference solution inside the glass is an aqueous solution. Furthermore, since MacInnes and Belcher have shown rather conclusively[2] that glass of the type used in this research contains water, it is exceedingly doubtful if the glass electrode will function at all correctly and reproducibly in any solvent but water.[8] It is somewhat possible that glasses might be made which would allow waterless hydrogen ions or protons[9] to migrate; in this case the glass electrode could be used in non-aqueous solutions provided only protons migrated through the glass.

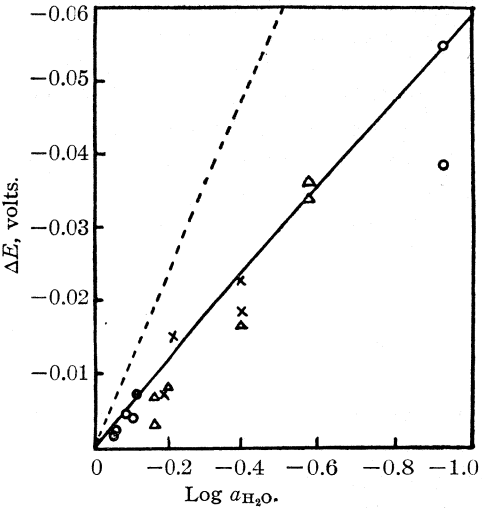


Fig. 4.—The errors of the glass electrode as a function of the activity of the water: circles, ethanol–water mixtures; crosses, HCl solutions; triangles, H_2SO_4 solutions; solid circles, 4.4 N LiCl. The solid line is theoretically calculated on the assumption that the hydrogen ion carries one molecule of water through the glass; the dotted line on the assumption of two water molecules per hydrogen ion. The exact proportionality between the potentials and the logarithm of the water activity shows that the glass may be considered as a water electrode.

The rôle of the glass electrode as a water electrode reduces the analogy between glass and quartz membranes which was apparent at the time of

[8] Professor Norris F. Hall has informed me that the glass electrode cannot be used in solutions of glacial acetic acid.

[9] The theoretical treatment of this paper indicates that the hydrogen ions do not migrate through the glass as protons as suggested by MacInnes and Belcher.[2]

writing of the author's last paper. Lengyel[10] conceives of glass electrodes of low electrical resistance as being explainable on purely thermodynamic grounds, but as the resistance of the glass is increased surface effects become more and more pronounced until with quartz membranes surface effects will predominate and a theory of adsorption of ions on the surface will serve to explain the potentials. However, this assumption has not been verified yet in any quantitative fashion. It would be interesting to see whether the quartz membranes will act as a water electrode similarly to the glass membranes. If they should also act as water electrodes, the adsorption theory would have to be abandoned inasmuch as it would be difficult to explain how a neutral molecule on adsorption could affect the potential.

Since the above paper was written, Lengyel has published further work on the quartz electrode[11] in which he has discovered errors of the quartz electrode in acid solutions similar to the glass electrode acid solution errors. He tried to explain these results on the basis of a consideration of the negative ions, but finds such an explanation inadequate. The author is unable to explain Lengyel's results quantitatively on the assumption that the quartz electrode acts as a water electrode although qualitatively the theory and the data are not irreconcilable.

Summary

1. The glass electrode is directly compared with the hydrogen electrode in acid solutions of sodium chloride and sulfate, lithium chloride, aluminum chloride and sulfate, hydrochloric acid, sulfuric acid and in acid ethanol water mixtures. A comparison was also made over a wide P_H range in a solution of sodium iodide dissolved in ethanol.

2. The errors of the glass electrode in acid solutions are not a direct function of the nature or concentration of any ion present. This statement includes the hydrogen ion.

3. The errors in alcoholic solutions are similar to the errors in acid solutions.

4. Previous theories to explain these errors are reviewed and rejected.

5. It is found that the acid solution errors are a function of the activity of the water; reduction of the activity of the water makes the error more negative in accordance with the equation

$$\Delta E = \frac{RT}{F} \ln a_{H_2O}$$

Because of this the glass electrode can be shown to act as a perfect *water electrode* at constant P_H (within the experimental uncertainties).

6. The mathematical analysis of the results indicates that as the hydrogen ion migrates through the glass it carries exactly one molecule of water

[10] Béla v. Lengyel, *Z. physik. Chem.*, **A153**, 425 (1931).

[11] Lengyel, *ibid.*, **A159**, 145 (1932); Lengyel and Mátrai, *ibid.*, **A159**, 393 (1932).

along with it. In other words, the hydrogen ion or proton is hydrated in the glass.

7. The results indicate that the glass electrode when made of the glass used in this research may not be used to measure the hydrogen ion activity of non-aqueous solutions.

8. By combining the equation for the glass electrode in acid solutions with the equation for the glass electrode in alkaline solutions given in the author's last paper, an equation for the glass electrode over an extensive P_H range is obtained.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RELATION BETWEEN THE TWO CONSTANTS OF THE ARRHENIUS EQUATION

BY MILTON J. POLISSAR

RECEIVED MARCH 23, 1932 PUBLISHED AUGUST 5, 1932

Introduction.—The rate constants of both first order and second order reactions can be represented by the following empirical equations

$$K = Se^{-Q/RT};\ \log K = B - Q/4.58T \qquad (1)$$

The simple collision hypothesis of gaseous bimolecular reactions yields the following equation for the second order rate constant

$$K = Ze^{-Q'/RT};\ \log K = \log Z - Q'/4.58T \qquad (2)$$

Z is proportional to the square root of the absolute temperature and is equal to the number of collisions between the reacting molecules, in moles per liter per second, when the concentration of each of the two reactants is one mole per liter. Q' is the heat of activation and for reactions measured at or near room temperature it is smaller than Q by about 300 calories. Equation 2 is the mathematical equivalent of the statement that all collisions between two reactant molecules in which the energy of impact is equal to or larger than the heat of activation will result in chemical decomposition.[1]

Several investigators tested the applicability of Equation 2 to second order rate constants in liquid solutions. In their calculations of the value of Z they assumed that the gas-kinetic formula may be relied upon to give the right order of magnitude for the number of collisions between the solute molecules. They found that the observed values of the tested rate constants were much smaller than those calculated by means of this formula.[2]

[1] *Cf.* Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, Oxford, 1929, pp. 100, 105.

[2] (a) Christiansen, *Z. physik. Chem.*, **113**, 35 (1924). (b) Norrish and Smith, *J. Chem. Soc.*, 129 (1928). (c) Moelwyn-Hughes and Hinshelwood, *ibid.*, 230 (1932).

In a recent paper Moelwyn-Hughes[3] listed a number of reactions in solution whose rate constants satisfy Equation 2. He also added several cases to the list of those reactions whose observed rate constants are much below the theoretical value. He was the first on record to make the observation that what he calls "normal" reactions are characterized by a heat of activation equal to about 21,000 calories, and that in other reactions the ratio between the calculated and the observed rates is the larger, the smaller the heat of activation. He tested several possible explanations of this parallelism and found them untenable, thus leaving the problem unsolved.

The object of the present contribution is to suggest an explanation of Moelwyn-Hughes' rule. It should be emphasized at this point that this explanation does not represent an attempt to reconcile the exceptions with the simple collision hypothesis. On the contrary, in the following discussion the point of view is taken that this hypothesis is too narrow to account for all known bimolecular reactions; attention is next called to the well-known fact that our restricted facilities for measuring rates in solution enable us to study only a fraction of all possible bimolecular reactions; finally, it is shown that all reactions suitable for investigation must satisfy the generalization announced by Moelwyn-Hughes.

The Present Status of the Simple Collision Hypothesis.—Hinshelwood[1] summarized in 1929 the then available data on gaseous bimolecular reactions. In six cases the observed rates agreed with those calculated by means of the simple collision hypothesis. In the seventh (the decomposition of ozone) the observed rate is higher than the calculated one. A few years ago it would have been difficult to explain a case in which the reaction takes place faster than the molecules can be activated by collisions. However, the modern theory of unimolecular reactions offers a simple explanation in the assumption that energy distributed among a large number of internal degrees of freedom can be converted into energy of activation.[4] Finally, the reaction between nitrogen pentoxide and ozone is a bimolecular one, and the observed rate of reaction is about 90,000 times as great as that allowed by the simple collision hypothesis. According to Hinshelwood, this may indicate a chain mechanism, but it may also be connected with the many degrees of freedom possessed by the complex $N_2O_5 \cdot O_3$.

No gaseous bimolecular reaction is known in which the observed rate is much smaller than that calculated by means of Equation 2.[4a] However, it was shown that the rates of reaction between triethylamine and ethyl iodide

[3] (a) Moelwyn-Hughes, *Chem. Rev.*, **10**, 241 (1932); (b) *Nature*, **129**, 316 (1932).

[4] Ref. 1, p. 152.

[4a] Just before this paper was sent to print the author's attention was called to the case of polymerization of ethylene in the gaseous phase. This is a bimolecular reaction, and its observed rate is one two-thousandth of that calculated [Pease, THIS JOURNAL, **53**, 613 (1931)].

and between acetic anhydride and ethyl alcohol in the gas phase are not much higher than the rates in non-polar solvents.[2c] The two reactions are bimolecular in solution, and it is very probable that they are of the same order in the gas phase. If their heats of activation are the same in the gas phase as in solution, then it follows from the available data that the rates calculated by means of Equation 2 are more than 100,000 times as large as the observed rates.

To summarize the evidence on the experimental side in the case of gaseous reactions, Equation 2 predicts correctly the rates of six known reactions; it gives too low values for two reactions and too high values for the last two reactions.

Equation 2 is derived on the assumption that all collisions in which the energy requirement is satisfied result in decomposition. Evidence from the field of unimolecular reactions throws some doubt on this assumption. The theory of unimolecular reactions is based on the fundamental assumption that the activated molecules are in thermal equilibrium with the unactivated ones. It follows that the average life of an activated molecule, with respect to decomposition, must be much larger than the average duration between two successive collisions. On the other hand, the time of contact between two colliding molecules is small in comparison with the duration between two successive collisions. It is not clear, then, why we must assume that in a bimolecular reaction all, or at least a large portion, of the activated collision complexes will undergo chemical decomposition during their relatively short life period. It seems more plausible that practically all complexes will separate into the original components and that only a small fraction will suffer decomposition.

On the Number of Collisions in Condensed Systems.—We can define with mathematical exactitude what we mean by a collision between two perfectly elastic and perfectly rigid spheres. With the use of statistical mechanics we can calculate the number of such collisions in a perfect hypothetical gas consisting of such ideal particles. If we pass to the case of a real gas, we lose some of the precision, but we are still in a position to calculate the number of collisions with an accuracy satisfactory enough for a kinetic interpretation of reaction rates. The introduction of an inert solvent gas in ordinary quantities does not call for a fundamental change in the collision formula. Unimportant corrections must be made to allow for the fact that the free space is reduced by the solvent particles and that intermolecular forces acquire an importance.

Let us suppose, however, that a sufficient quantity of the solvent gas is introduced to pack the space solidly with molecules. Under such conditions each of the solute molecules is in continuous contact with several solvent molecules. A definite portion of the solute molecules of the first kind are in continuous contact with molecules of the second kind. Evi-

dently, neither our usual definition of "collision" nor our usual formula for the number of collisions can be employed without making some fundamental changes in them. The mere application of the free-space correction factor is insufficient, since molecules having ordinary dimensions cannot move in such "free" space.

There is good evidence of the fact that molecules in the liquid phase are fairly closely packed. Thus, if we calculate the molecular diameters of molecules in the liquid phase on the assumption of close packing, we obtain values which are in fair agreement with those obtained by other methods.[5] It follows from what has been said that the application of the gas-kinetic formula to the case of solutions may be incorrect not only in degree but also in kind.[6]

It was shown that on the empirical side the universal applicability of Equation 2 to gaseous bimolecular reactions is far from established; on the theoretical side there is no *a priori* reason why the rate of a reaction cannot be much smaller than that predicted by this equation; furthermore, this equation cannot even be relied upon to give the maximum limit for the rate of a bimolecular reaction at least in the case of molecules with a large number of internal degrees of freedom; finally, it was shown that the application of this equation in the case of liquid solutions is objection-

[5] Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1925, p. 332.

[6] The question may be raised as to the nature of the process whereby molecules in a closely packed system change neighbors and position. The answer will probably be supplied by the statistical theory of fluctuations. As long as the molecules are not solidly packed, there is room for fluctuation in density. The fluctuation in a system consisting of a large number of molecules is very small. However, in a system consisting of from ten to fifty molecules the fluctuation may be violent enough to allow individual molecules a frequent change of neighbors and of position.

It should be pointed out that in a closely packed system bimolecular reactions call for second order rate equations, without the introduction of the idea of collisions. Thus, if we assume that in a dilute solution of substances A and B each molecule of solute A is in contact with eight other molecules most of the time, we arrive at the following formula for the concentration of the AB complex, in moles per liter

$$n_{AB} = 8s_2C_AC_B/n$$

where n is the number of moles of solution per liter (in a very dilute solution it is equal to the number of moles of solvent per liter); C_B/n is the molal fraction of B; s_2 is a statistical factor depending on the relative affinity between molecules A and the other molecules in solution; it is nearly equal to unity when the molecules of B and of the solvent are similar; it is much larger than unity if A and B are oppositely charged ions, and it is much smaller than unity if they are ions carrying charges of the same sign.

If k_2 is the probability that complex AB will undergo decomposition in the course of one second, then the rate of reaction is given by the equation

$$r_2 = 8k_2s_2C_AC_B/n$$

Similarly, the rate of a termolecular reaction is given by the following equation

$$r_3 = 56k_3s_3C_AC_BC_C/n^2$$

able because of the fact that "collisions" in solution are of a nature entirely different from that of collisions in the gas phase. One should not therefore be surprised to find a large number of cases which are not in agreement with Equation 2.

The *ad hoc* nature of the simple collision hypothesis was clearly recognized in the earlier discussions.[7] However, in a series of recent papers there is shown a definite tendency to assume that conformity with Equation 2 is the normal rule, and elaborate *ad hoc* explanations are offered to reconcile the "exceptions" with the rule.[2c,3,8] While one may criticize this tendency, there is no doubt that Moelwyn-Hughes' generalization regarding the parallelism between the heat of activation and the deviation from Equation 2 is well grounded. An explanation of this relation is offered in the following section.

The Relation between the Values of B and Q for Investigated Bimolecular Reactions in Liquid Solutions.—The study of reactions in solution is confined to a small range of temperatures. For this reason the value of log Z does not vary much from one reaction to another and is approximately equal to 11. Equation 2 can therefore be replaced by

$$\log K = 11 - Q'/4.58T \qquad (3)$$

Moelwyn-Hughes' generalization is equivalent to the statement that the value of B in Equation 1 is much smaller than 11 for those reactions in which the value of Q is much smaller than 21,000 calories. It is also equivalent to an empirical generalization made by Holzschmidt,[9] who found a linear relationship between B and Q.

If we search for the relation between the values of B and Q which is characteristic of all reactions having measurable speeds at ordinary temperatures, we shall find the solution in Equation 1. Thus, if a reaction is to have a value of log K which is not much different from some measurable value log K_1, at a temperature T which is not far removed from some average temperature T_1, then the two Arrhenius parameters of this reaction must satisfy approximately the equation

$$\log K_1 = B - Q/4.58T_1 \qquad (4)$$

The B and Q values of all reactions investigated by ordinary methods must satisfy approximately such a linear equation. An inspection of Equation 4 will show that if the pair of values ($B = 11$, $Q = 21{,}000$) forms an approximate solution, then in other solutions $B \ll 11$ if $Q \ll 21{,}000$.

Figure 1 will be used to illustrate the relation developed in this section. It is a log K *vs.* $1/T$ plot for seven reactions measured by direct methods and

[7] Ref. 1, p. 100.

[8] For the extension of the simple collision hypothesis to the case of first order reactions in solution see Moelwyn-Hughes, *J. Chem. Soc.*, 95 (1932); Moelwyn-Hughes and Rolfe, *ibid.*, 241 (1932).

[9] Holzschmidt, *Z. anorg. allgem. Chem.*, **200**, 82 (1931).

three reactions investigated by indirect methods. The short segments within the small rectangle represent the temperature regions within which measurements were actually made. The light lines outside the rectangle are the graphical equivalent of the extrapolation by means of which the

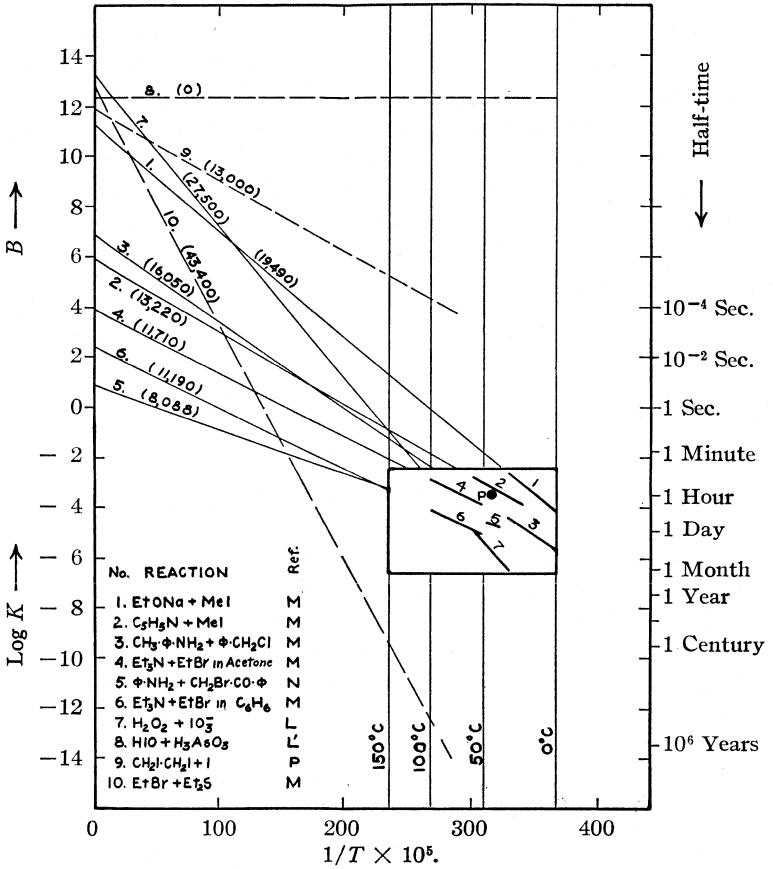


Fig. 1.—The relative size of the field within which the great majority of reactions in solution had been studied. Reactions with large values of B and small values of Q, or with small values of B and large values of Q, are ordinarily not to be found in the literature, since their Arrhenius lines do not cross the small rectangle.

References: M., Moelwyn-Hughes; N., Norrish and Smith; L., Liebhafsky, THIS JOURNAL, **53**, 896 (1931); P., Polissar.

value of B is obtained. The slope of each line is equal to $Q/4.58$. The intercept on the log K axis is equal to B. The respective values of Q are marked along each line. The scale of ordinates on the right gives for each value of K the half-time of reactions in which the initial concentrations of the two reactants are one mole per liter. The small rectangle was

drawn in to show broadly the region within which the great majority of measurements of reaction rates in solution had been carried out.

It is evident that all reactions suitable for direct investigation have the common characteristic that their Arrhenius lines cross the small rectangle. An inspection of Fig. 1 will show that for such reactions small values of Q must be coupled with small values of B. Thus, reaction 9 cannot be studied by ordinary methods, since its rates at ordinary temperatures are too high.[10]

While it is true that reactions whose Arrhenius lines are far removed from the rectangle cannot be measured directly, it would be erroneous to assume that they cannot be measured at all. Thus, the data for the three broken lines in Fig. 1 were obtained by indirect methods. Line 10 (the reaction between ethyl bromide and diethyl sulfide) was obtained from a study of the reverse reaction and the reaction isochore.[3a] The position of line 9 (the catalytic decomposition of ethylene iodide in the presence of atomic iodine) was estimated from the kinetics of the decomposition in the presence of iodine and the degree of dissociation of molecular iodine.[11] Finally, the data for line 8 (the reaction between hypoiodous and arsenious acids) were obtained from measurements of the rate of reaction between iodine and arsenious acid, in the presence of hydriodic acid.[12] It is hardly necessary to add that the usefulness of the three reactions as examples of cases investigated by indirect methods is independent of the fact that the kinetic interpretations given by the three authors may be tentative.

Summary

A critical examination of the simple collision hypothesis leads to the conclusion that the latter is too narrow to account for all known bimolecular reactions.

Attention is called to the fact that the application of the gas-collision formula to the case of liquid solutions may be incorrect not only in degree but also in kind.

A simple explanation is offered of the linear relationship between the two Arrhenius constants of bimolecular reactions in solution.

BERKELEY, CALIFORNIA

[10] If all the lines were to pass through a point P inside the rectangle, their B–Q value would have to satisfy Equation 4, with K_1 and T_1 equal to the coördinates of point P. Since the lines pass near that point but not through it, the pairs of values satisfy only approximately a common linear equation. Point P was not selected arbitrarily; its coördinates were chosen in such a way as to give the equation of Holzschmidt's line when substituted in (4). Allowance had to be made for the fact that Holzschmidt used the minute, and not the second, as the unit of time.

[11] Polissar, THIS JOURNAL, **52**, 956 (1930).

[12] Liebhafsky, *J. Phys. Chem.*, **35**, 1648 (1931).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE IONIC ACTIVITY COEFFICIENT PRODUCT AND DISSOCIATION OF WATER IN BARIUM CHLORIDE SOLUTIONS AT 25°

BY HERBERT S. HARNED AND C. MORGAN MASON[1]

RECEIVED MARCH 24, 1932 PUBLISHED AUGUST 5, 1932

The equilibrium constant, K, of the dissociation of water is given by

$$K = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_H m_{OH} \qquad (1)$$

where the "γ's" and "m's" are the activity coefficients and molal concentrations of the ions denoted by subscripts, and a_{H_2O} is the activity of the water. The quantities $\gamma_H\gamma_{OH}/a_{H_2O}$ and, subsequently, $m_H m_{OH}$ have been evaluated from suitable electromotive force measurements for the cases of aqueous cesium,[2] potassium, sodium[3] and lithium chloride[4] solutions and potassium and sodium bromide[5] solutions in earlier investigations. The present study is concerned with the evaluation of these important quantities in aqueous solutions of barium chloride by two methods which involve somewhat different cells and computations.

The Determination of the Ionic Activity Coefficient and Dissociation of Water in Aqueous Barium Chloride Solutions by Method I.—The electromotive forces at 25° of the cells

$$H_2 \mid Ba(OH)_2\ (m_1),\ BaCl_2\ (m_2) \mid Ba_xHg \mid Ba(OH)_2\ (m_0) \mid H_2 \qquad I$$

are given by the equation

$$E = 0.08873 \log \frac{\gamma_{(m_1+m_2)}}{\gamma_{m_0}} \frac{\sqrt[3]{m_1^2(m_1+m_2)}}{m_0} + 0.05915 \log \frac{p_{m_0}}{p_{m_1+m_2}} \qquad (2)$$

$\gamma_{m_1+m_2}$ is the activity coefficient of barium hydroxide, $\sqrt[3]{\gamma_{Ba}\gamma_{OH}^2}$, in the solution of barium chloride, and γ_{m_0} is the same quantity at a concentration m_0 in the aqueous solution on the right of the cell which we have employed as reference and kept at a constant concentration of 0.05 M. p_{m_0} and $p_{m_1+m_2}$ are the vapor pressures of water in the reference solution and in the hydroxide–chloride solutions, respectively. From previous results,[6] we know that γ_{m_0} equals 0.527, and, consequently, from measurements of the above cells we may determine $\gamma_{(m_1+m_2)}$ if we evaluate the term in equation (2) which contains the ratio of the vapor pressures.

The technique employed in these measurements has been described by

[1] This paper was constructed from material forming part of a dissertation presented to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

[2] Harned and Schupp, THIS JOURNAL, **52**, 3892 (1930).

[3] Harned, *ibid.*, **47**, 930 (1925).

[4] Harned and Swindells, *ibid.*, **48**, 126 (1926).

[5] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

[6] Harned and Mason, THIS JOURNAL, **54**, 1439 (1932).

Harned and Mason. It is desirable to record the electromotive forces for cells containing barium hydroxide at the same concentration on both sides. Since the solutions were boiled *in vacuo*, it was necessary to apply a small correction in order to accomplish this result. A concentration of m_0 and m_1 equal to 0.05 was found to be convenient.

Table I contains the experimental results and the computed values of the vapor pressure ratios as well as the values of $\gamma_{m_1+m_2}$. The second and third columns contain the observed electromotive forces and those read from a smooth curve drawn through them, respectively. The consistency of the results is thus seen to be good considering the difficulties of measurement of cells of this type. The fourth column contains the ratios of the vapor pressure of pure water to that of a barium chloride solution of concentration $(m_2 + 0.05)$ which we employed to compute γ. These were computed from the activity coefficients of barium chloride by the method described by Harned.[7] The activity coefficients employed in evaluating the constants of Harned's equation were obtained from the electromotive force measurements of Lucasse.[8] The equation

$$\log \gamma = -\beta m^{\alpha'} + \alpha m \qquad (3)$$

was found to give satisfactory agreement with the observed activity coefficients when α, α' and β were taken to be 0.435, 0.381 and 0.835, respectively, and, consequently, the vapor pressure ratios may be obtained by the equation

$$\ln \frac{p_0}{p_m} = \frac{m}{55.5}\left[\nu + \frac{2.303\ \alpha\nu m}{2} - \frac{2.303\ \nu\beta\alpha'}{\alpha' + 1} m^{\alpha'}\right] \qquad (4)$$

By rearrangement of equation (2) we obtain

$$\log \gamma_{m_1+m_2} = \frac{E}{0.08873} + \log \gamma_0 m_0 - \frac{1}{3}\log m_0^2(m_0 + m_2) - \frac{2}{3}\log \frac{p_0}{p_{(m_0+m_2)}} \qquad (5)$$

by means of which the values of $\gamma_{(m_1+m_2)}$ given in the fifth and sixth columns of Table I were computed. We note at this juncture that the values of $p_{m_0+m_2}$ are those of pure aqueous barium chloride solutions at the concentration $(m_0 + m_2)$. These have been used in place of the vapor pressures of the solutions containing m_0 barium hydroxide and m barium chloride. This procedure causes no large error since the last term on the right of equation (5) is small at low concentrations, and since at high concentrations there is present many times more barium chloride than hydroxide.

In Fig. 1, the values of the activity coefficient of barium hydroxide in barium chloride solutions as well as in pure aqueous solution have been

[7] See Taylor, "Treatise on Physical Chemistry," first ed., D. Van Nostrand Co., New York, 1924, Vol. II, pp. 751–753.

[8] Lucasse, THIS JOURNAL, **47**, 743 (1925); Harned, *ibid.*, **48**, 326 (1926); see table in Taylor, "Treatise on Physical Chemistry," second ed., D. Van Nostrand Co., New York, 1930, Vol. I, p. 772, Table IX.

TABLE I

THE ACTIVITY COEFFICIENT OF BARIUM HYDROXIDE IN AQUEOUS SOLUTIONS OF BARIUM CHLORIDE AT 25° FROM MEASUREMENTS OF THE CELLS

$H_2 \mid Ba(OH)_2(0.05), BaCl_2(m_2) \mid Ba_xHg \mid Ba(OH)_2(0.05) \mid H_2$

m_2	$E_{exp.}$	E_{curve}	$\frac{p_0}{p_{m_0+m_2}}$	$\gamma_{(m_1+m_2)}$ (obs.)	$\gamma_{(m_1+m_2)}$ (curve)
0.0	0.0000	0.0000	1.0015	(0.527)	(0.527)
.02096	.0014	.0014	1.0032	.488	.488
.03076	.0024	.0024	1.0036	.477	.476
.04881	.0034	.0033	1.0044	.458	.457
.05148	.0034	.0034	1.0046	.454	.454
.07219	.0041	.0042	1.0054	.434	.435
.09175	.0046	.0046	1.0063	.418	.418
.09427	.0046	.0047	1.0065	.416	.417
.1044	.0048	.0049	1.0068	.409	.410
.2012	.0063	.0064	1.0111	.360	.361
.2974	.0075	.0072	1.0155	.332	.330
.4025	.0081	.0080	1.0206	.308	.307
.4926	.0086	.0084	1.0253	.293	.291
.4979	.0081	.0084	1.0255	.288	.290
.5933	.0087	.0088	1.0308	.276	.277
.6981	.0091	.0091	1.0370	.265	.265
.7928	.0091	.0094	1.0512	.252	.254
.8686	.0098	.0096	1.0525	.249	.248
.9091	.0101	.0099	1.0531	.247	.246
1.0145	.0103	.0102	1.0549	.240	.239
1.2530	.0102	.0109	1.0779	.220	.224

plotted against the square root of the ionic strength. We note that the values of γ in the salt solutions are higher than in the pure aqueous solutions.

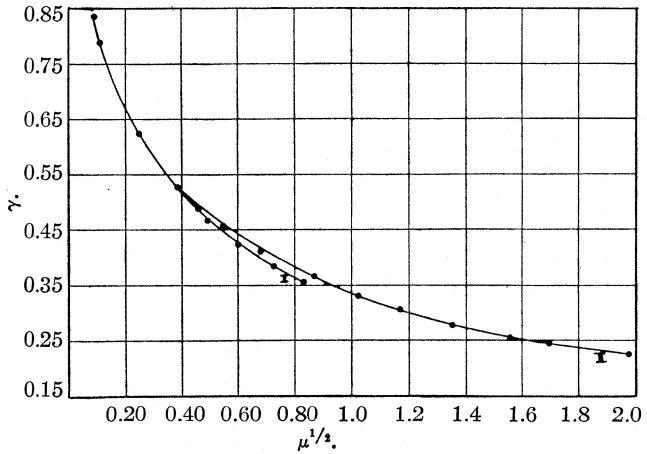


Fig. 1.—The activity coefficient of barium hydroxide in water and in aqueous barium chloride solutions: I, water; II, barium chloride solutions.

To obtain $\gamma_H\gamma_{OH}/a_{H_2O}$ in the barium chloride solution by this method, it is necessary to know both the activity coefficient of hydrochloric acid at zero concentration, and the activity coefficient of barium hydroxide at zero concentration in a barium chloride solution of m molal concentration. Further, the activity coefficient of barium chloride in aqueous solution at a concentration m, and the activity of water in this solution are required. Thus, all the necessary quantities will be known in the same solution and from them $\gamma_{Ba}\gamma^2_{OH}/a^2_{H_2O}$, $\gamma_H\gamma_{Cl}$ and $\gamma_{Ba}\gamma^2_{Cl}$ may be computed. From these quantities $\gamma_H\gamma_{OH}/a_{H_2O}$ may be readily computed by the equation

$$K_\gamma = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = \sqrt{\frac{\gamma_{Ba}\gamma^2_{OH}\gamma^2_H\gamma^2_{Cl}}{a^2_{H_2O}\gamma_{Ba}\gamma^2_{Cl}}} \qquad (6)$$

The evaluation of $\gamma_{Ba}\gamma^2_{OH}/a^2_{H_2O}$, to be denoted $\gamma''_{Ba(OH)_2}$ and $\gamma_H\gamma_{Cl}$, in the pure barium chloride solutions was carried out by a graphical method which is illustrated by Figs. 2 and 3. The results are given in Table II.

TABLE II

THE CALCULATION OF THE IONIC ACTIVITY COEFFICIENT PRODUCT OF WATER IN BARIUM CHLORIDE SOLUTIONS

	$\gamma''_{Ba(OH)_2}$			γ_{HCl}			γ_{BaCl_2}	K_γ
μ	(1)	(2)	(3)	(4)	(5)	(6)		
0.01	0.809	...	0.809	0.902	0.902	0.891	0.795[a]	0.815
.05	.652	...	.649	.829	.821	.818	.670	.638
.1	.570	...	.574	.796	.778	.776	.589	.577
.2	.489	0.498	.506	.766	.741	.739	.526	.515
.5	.390	.404	.411	.757	.704	.702	.454	.415
.7	.357	.373	.378	.771	.700	.699	.430	.403
1.0	...	.339	.343	.810	.700	.699	.411	.373
1.5	...	.299	.301	.903	.714	.713	.395	.338
2.0	...	.276	.279	1.019	.738	.737	.392	.327
2.5	...	.261	.264	1.151	.777	.776	.394	.331
3.0	...	.253	.256	1.320	.826	.825	.398	.351
3.5	...	.245	.248	1.520	.881	.879	.403[a]	.373
4.0	...	.236	.238	1.762	.935	.934	.406[a]	.392

(1) $\gamma''_{Ba(OH)_2}$ in aqueous solution. (2) $\gamma''_{Ba(OH)_2}$ (0.05) in barium chloride solutions. (3) $\gamma''_{Ba(OH)_2}$ (0.00) in barium chloride solutions. (4) γ_{HCl} in aqueous solutions. (5) γ_{HCl} (0.01) in barium chloride solutions. (6) γ_{HCl} (0.00) in barium chloride solutions.

[a] Extrapolated points.

In Fig. 2, the values of log γ'' are plotted against the concentration of barium hydroxide. The curve represents the activity coefficient of the hydroxide in aqueous solution and was obtained from the values in the second column of Table II and the points represented by the filled in circles are those taken from the third column. To extrapolate these latter results to zero hydroxide concentration, use was made of the law of the linear variation of the logarithm of the activity coefficient which states that at con-

stant total ionic strength log γ varies linearly with the concentration of the substance whose activity coefficient is γ. Thus, by drawing straight lines from the curve through the point at the same total concentration of electrolyte, the extrapolation may be effected. Unfortunately, the saturated solution of barium hydroxide is at too low a concentration to accomplish this at all ionic strengths. Consequently, we have resorted to the expedient of drawing a system of parallel lines from the point to the ordinate, and reading from the curve the results given in the fourth column of the table. Figure 3 shows an exactly similar plot of the log γ_{HCl} against the concentration of the acid. The curve is drawn through the points taken from the computations and data of Randall and Young[9] given in the fifth column of the table. The points near the ordinate through which the straight lines at constant ionic strength are drawn represent the activity coefficients of hydrochloric acid in barium chloride solutions determined by Harned and Robinson[10] and given in the sixth column. In this case, the parallel nature of such plots is very apparent. The extrapolated values of γ_{HCl} are given in the seventh column. The values of the activity coefficient of barium chloride in aqueous solution given in the eighth column were those computed from the amalgam cell measurements of Lucasse.[11] The last column contains K_γ computed from the results in the fourth, seventh and eighth columns by equation (6).

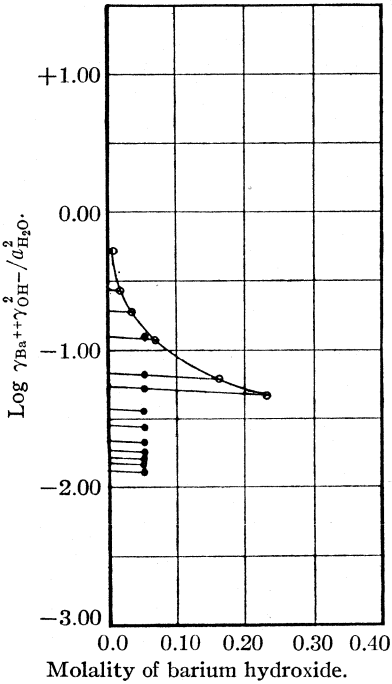


Fig. 2.—Plots of log γ'' against m_1 at constant total ionic strength.

The Evaluation of $K\gamma$ by the Second Method.—The electromotive forces of the cells at 25°

$$H_2 \mid Ba(OH)_2\ (m_0),\ BaCl_2\ (m) \mid AgCl \mid Ag \qquad \text{II}$$

are given by the equation

$$E = E_0 - 0.05915 \log \gamma_H \gamma_{Cl} m_H m_{Cl} \qquad (7)$$

and the dissociation constant, K_w, of water is

$$K_w = \frac{\gamma_H \gamma_{OH} m_H m_{OH}}{a_{H_2O}} \qquad (8)$$

[9] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

[10] Harned and Robinson, *ibid.*, **50**, 3157 (1928).

[11] Lucasse, *ibid.*, **47**, 743 (1925).

By eliminating m_H from these equations, rearranging terms, and substituting 0.2224 for the normal potential of hydrochloric acid, E_0,[12] we obtain

$$\left[E - 0.2224 + 0.05915 \log \frac{m}{m_0}\right] = -0.05915 \log K_w a_{H_2O} - 0.05915 \log \frac{\gamma_H \gamma_{Cl}}{\gamma_H \gamma_{OH}} \quad (9)$$

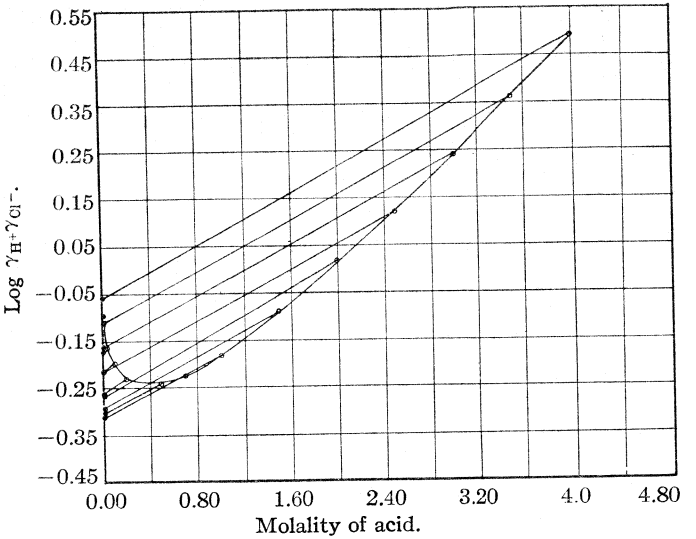


Fig. 3.—Plots of log $\gamma_H\gamma_{Cl}$ against the acid molality in barium chloride solutions of a constant total ionic strength.

The actual measurements of the cells are given in Table III. The number of cells at the concentrations designated in the first three columns which were measured is given in column four and the difference in millivolts in column five. Column six contains the mean values of the electromotive forces and column seven the value of the left side of equation (9).

In order to obtain results at convenient concentrations, the values of the left side of equation (9) were plotted against μ as shown in Fig. 4. Since a_{H_2O}, $\gamma_H\gamma_{Cl}$ and $\gamma_H\gamma_{OH}$ equal unity at zero ionic strength, the value of the ordinate at zero μ equals $-0.05915 \log K_w$. Since the present results were not carried out at sufficiently low concentrations to obtain an accurate extrapolation, we have drawn the curve to 0.8280, corresponding to a value of K_w equal to 1.005×10^{-14}.[13]

The second column of Table IV contains the values of $E - E_0 + 0.05915$

[12] Roberts, THIS JOURNAL, **52**, 3877 (1930); Harned and Schupp, Jr., *ibid.*, **52**, 3892 (1930); Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[13] This value, which was obtained by Lewis and Randall ["Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 434] is very close to the value recently obtained in this Laboratory and will be employed until the more recent results can be published.

TABLE III

THE ELECTROMOTIVE FORCES OF THE CELLS

H_2 | $Ba(OH)_2$ (m_0), $BaCl_2$ (m) | AgCl | Ag, at 25°

m_0	m	μ	No. of cells	Δ(mv.)	E	$\left[E - E_0 + 0.05915 \log \frac{m}{m_0}\right]$
0.05058	0.01067	0.1838	2	0.01	1.0883	0.8259
.05043	.02027	.2121	2	.15	1.0715	.8257
.05088	.02023	.2133	2	.05	1.0719	.8258
.05052	.02125	.2153	2	.5	1.0702	.8256
.05019	.03148	.2450	2	.06	1.0602	.8258
.05149	.03156	.2491	2	.07	1.0607	.8257
.05092	.04988	.3024	2	.03	1.0483	.8254
.05014	.07174	.3656	2	.03	1.0381	.8249
.05027	.09620	.4394	2	.06	1.0302	.8245
.05088	.1028	.4610	2	.04	1.0287	.8244
.04912	.1912	.7210	2	.06	1.0095	.8220
.05073	.2053	.7681	2	.06	1.0090	.8225
.05049	.3012	1.0551	2	.00	0.9972	.8207
.05040	.4071	1.3725	2	.01	.9875	.8188
.05020	.5120	1.6569	2	.01	.9808	.8176
.05105	.6115	1.9877	2	.01	.9741	.8155
.05026	.6863	2.2097	2	.04	.9696	.8144
.05007	.7855	2.5067	2	.01	.9647	.8130
.05096	.8145	2.5964	2	.07	.9638	.8126
.05017	.9017	2.8556	2	.06	.9593	.8111
.05030	.9124	2.8881	2	.06	.9587	.8107
.05081	1.0079	3.1761	2	.03	.9554	.8097
.05092	1.2444	3.8808	2	.15	.9460	.8072
.04920	1.3171	4.1041	1	..	.9455	.8067

TABLE IV

CALCULATION OF K_γ FROM THE DATA IN TABLE III, AND VALUES OF m_w, $\gamma_H\gamma_{OH}$, AND $\sqrt{\gamma_H\gamma_{OH}}$ COMPUTED AT ROUND CONCENTRATION

μ	$\left[E - E_0 + 0.05915 \log \frac{m}{m_0}\right]$ (1)	K_γ (1)	K_γ (2)	$m_w \times 10^7$ (1)	$m_w \times 10^7$ (2)	$\gamma_H\gamma_{OH}$ (1)	$\gamma_H\gamma_{OH}$ (2)	γ (1)	γ (2)
0.01	0.8279	0.815	0.792	1.11	1.13	0.815	0.793	0.903	0.890
.05	.8276	.638	.660	1.26	1.23	.637	.659	.798	.813
.1	.8272	.577	.582	1.32	1.31	.576	.581	.759	.762
.2	.8264	.515	.514	1.40	1.40	.513	.512	.716	.717
.5	.8242	.415	.426	1.56	1.54	.412	.423	.642	.651
.7	.8229	.403	.401	1.58	1.58	.398	.397	.630	.630
1.0	.8210	.373	.373	1.64	1.64	.367	.368	.606	.607
1.5	.8180	.338	.345	1.72	1.71	.330	.337	.575	.581
2.0	.8154	.327	.335	1.75	1.73	.316	.325	.562	.570
2.5	.8129	.331	.335	1.74	1.73	.317	.321	.563	.566
3.0	.8104	.351	.343	1.69	1.71	.333	.325	.577	.570
3.5	.8085	.373	.361	1.64	1.67	.349	.339	.591	.582
4.0	.8069	.392	.384	1.60	1.62	.362	.355	.602	.596

(1) Method I. (2) Method II.

log (m/m_0) read from the plot of Fig. 4. K_γ may now be readily calculated as can be seen by rearranging (9) as follows

$$\log K_\gamma = \log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log (m/m_0)}{0.05915} + \log K + \log \gamma_H \gamma_{Cl} \qquad (9a)$$

$\gamma_H \gamma_{Cl}$ is the activity coefficient product of hydrochloric acid in the barium chloride solutions or the square of γ_{HCl} given in the seventh column of Table II. The values of K_γ thus obtained are given in the fourth column

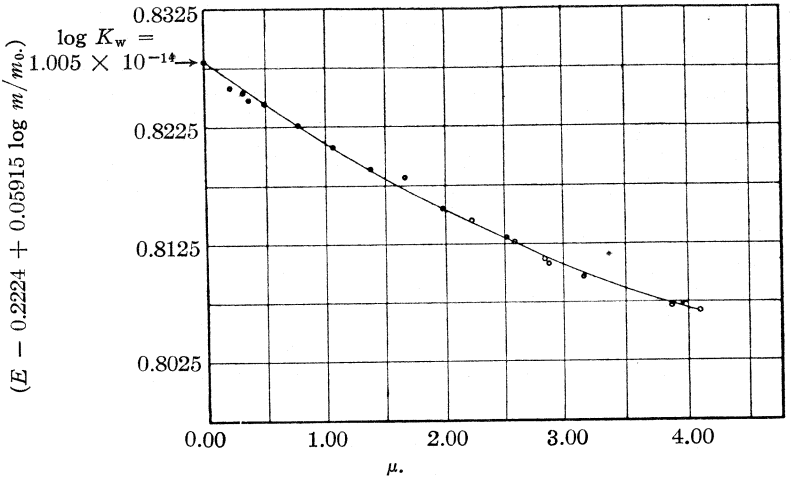


Fig. 4.—Plot of the values of the left side of equation (9) against ionic strength.

of Table IV. In the third column the values of K_γ obtained by the first method are given for purposes of comparison. Both series of values are

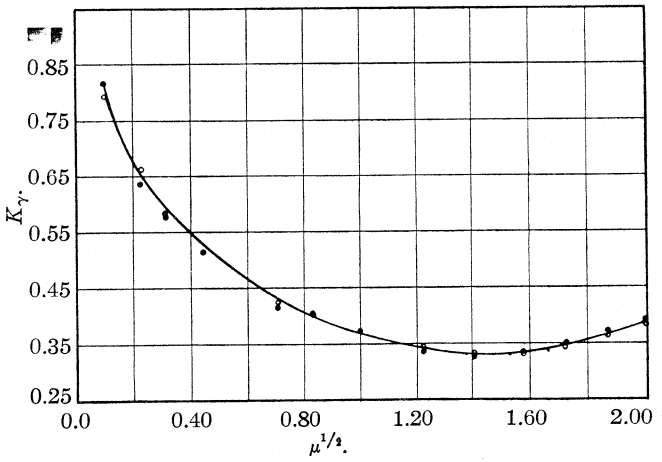


Fig. 5.—Plot of the ionic activity coefficient product, of water, K_γ, in barium chloride solutions: ●, method I; ○, method II.

plotted against $\mu^{1/2}$ in Fig. 5. The agreement is excellent when we consider the difficulties involved in measuring cells containing barium amalgam.

The fifth and sixth columns of Table IV contain the values of $m_w = m_H = m_{OH}$ computed by equation (8). The next two columns contain the values of $\gamma_H \gamma_{OH}$ computed by multiplying K_γ by a_{H_2O}, and the last two columns γ or $\sqrt{\gamma_H \gamma_{OH}}$. The values of γ obtained by the two methods rarely differ by more than 1% or ± 0.5% from their mean.

Summary

1. Measurements of the electromotive forces of the cells

$$H_2 \mid Ba(OH)_2\ (m_1),\ BaCl_2\ (m_2) \mid Ba_xHg \mid Ba(OH)_2\ (m_0) \mid H_2$$

have been made, and the activity coefficient of barium hydroxide in aqueous barium chloride solutions has been computed.

2. From these and other suitable results previously determined, the ionic activity coefficient of water in barium chloride solutions has been computed.

3. The cells

$$H_2 \mid Ba(OH)_2\ (m_0),\ BaCl_2\ (m) \mid AgCl \mid Ag$$

have been measured and the ionic activity coefficient of water has been computed from the results, and compared with the values obtained from the amalgam cells.

4. The dissociation of water in barium chloride solutions increases, passes through a maximum and then decreases with increasing ionic strength, a behavior similar to that observed in solutions of the alkaline halides. The maximum dissociation occurs at 1.5μ.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, CHEMICAL LABORATORY OF THE BAVARIAN ACADEMY OF SCIENCES, MUNICH, GERMANY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA]

INTEGRAL HEATS OF DILUTION AND RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM BROMIDE AND POTASSIUM BROMIDE SOLUTIONS AT TWENTY-FIVE DEGREES*

BY H. HAMMERSCHMID AND A. L. ROBINSON

RECEIVED APRIL 1, 1932 PUBLISHED AUGUST 5, 1932

Introduction

The measurement of heats of dilution of strong electrolytes at concentrations low enough to permit an unambiguous extrapolation of the results to infinite dilution makes possible a combination of such measurements with data obtained at higher concentrations to calculate the relative partial molal heat contents of the components of the solutions. These are the partial molal heat contents referred to the molal heat contents of

* Communication Number 37 on Thermochemical Investigations by E. Lange and co-workers.

the reference state, the infinitely dilute solution.[1] A knowledge of the partial molal heat contents and the partial molal specific heats of the components of solutions is necessary for the calculation of thermochemical and thermodynamic properties of solutions, such as heats of reaction and their temperature coefficients, temperature coefficients of activity coefficients and partial molal free energies, temperature coefficients of solubility and ionic entropies.

Measurements are presented here of the heats of dilution of aqueous sodium bromide and potassium bromide solutions from 0.1 *M* to infinite dilution at 25° and these measurements are combined with data of Wüst and Lange[2] to calculate relative partial molal heat contents from infinite dilution to saturation.

Experimental

A differential adiabatic calorimeter, developed by Lange and co-workers, already described[3] was employed. All details of manipulation and calculation were the same as in previous investigations.

The potassium bromide was a guaranteed preparation of de Haën, several times recrystallized. For the sodium bromide measurements two different 0.1 *M* stock solutions were used; one was a solution prepared by Dr. W. Geffken for density determinations and kindly furnished by him, which contained sodium bromide prepared from pure sodium carbonate,[4] and solution two was made from a Kahlbaum preparation that had been recrystallized twice. Both solutions were standardized by titration with two different silver nitrate solutions using phenosafranine as an indicator.[5]

The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The third column of the table gives the heat effects of individual measurements (negative values of ΔH indicate heat evolved) in this concentration interval calculated per mole of salt, and the fourth column gives the average of the individual measurements and the probable error, exclusive of any systematic errors. The reproducibility of the measurements is better than two per cent.

Discussion

The data of Table I are plotted against the square root of the molality (weight and volume concentrations differ inappreciably in this concen-

[1] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 88.

[2] Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

[3] Lange and Monheim, *ibid.*, **149A**, 51 (1930); Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

[4] Baxter, THIS JOURNAL, **38**, 70 (1916).

[5] Fajans and Wolff, *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

TABLE I

MEASURED HEATS OF DILUTION AT 25°

Initial concn., mole/liter	End concn., mole/liter	ΔH, calories/mole Prep. 1		Prep. 2		Average ΔH, calories/mole
		Sodium Bromide				
0.1	0.0026	−51.3	49.7	51.9	52.3	−51.3 ± 0.3
.1	.0052	−45.5	45.9	45.3	46.3	−45.8 ± .15
.05	.0013	−49.9	49.4	49.3	50.0	−49.7 ± .1
.05	.0026	−44.1	44.1	44.0	43.9	−44.0 ± .0
.025	.00065	−43.0	43.1	43.6		−43.2 ± .1
.025	.0013	−38.5	38.4	39.2		−38.7 ± .2
.0125	.00065	−31.5	32.3	30.2	30.6	−31.4 ± .3
.0125	.000328	−34.4	35.0	33.6	34.7	−34.4 ± .2
.00627	.000164	−22.4	24.3	24.4		−23.7 ± .4
.00627	.000325	−21.7	22.7	22.6		−22.3 ± .2
		Potassium Bromide				
0.1	0.0026	−44.6	43.0	43.5	43.5	−43.7 ± 0.2
.1	.0052	−37.0	36.0	37.0		−36.7 ± .2
.05	.0013	−40.5	41.0	41.1		−40.9 ± .1
.05	.0026	−35.7	35.9	37.2	36.2	−36.3 ± .2
.025	.00065	−38.1	41.0	37.9	38.7	−38.9 ± .3
.025	0013	−33.8	33.2	33.8		−33.6 ± .2
.0125	.000329	−30.9	31.1	31.4	30.6	−31.0 ± .1
.0125	.00065	−28.9	29.0			−29.0 ± .05

tration range) in Fig. 1. Below 0.01 M the integral heats of dilution are proportional to $m^{1/2}$ within the limit of experimental error and can be extrapolated to infinite dilution with an uncertainty of not more than one calorie. In Fig. 2 the results below 0.1 M have been combined with the data of Wüst and Lange which extend to saturation for both salts. The error involved in coördinating the two sets of measurements is not more than five calories and is probably less. In Table II are given the integral heats of dilution for the two salts at various concentrations from infinite dilution up to saturation; these values have been interpolated from Figs. 1 and 2. Up to 0.01 M the integral heat of dilution (heat absorbed when a solution containing one mole of the salt is diluted with an infinite amount of water)

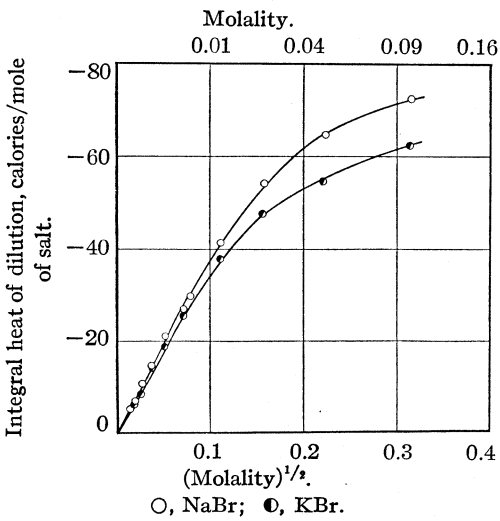
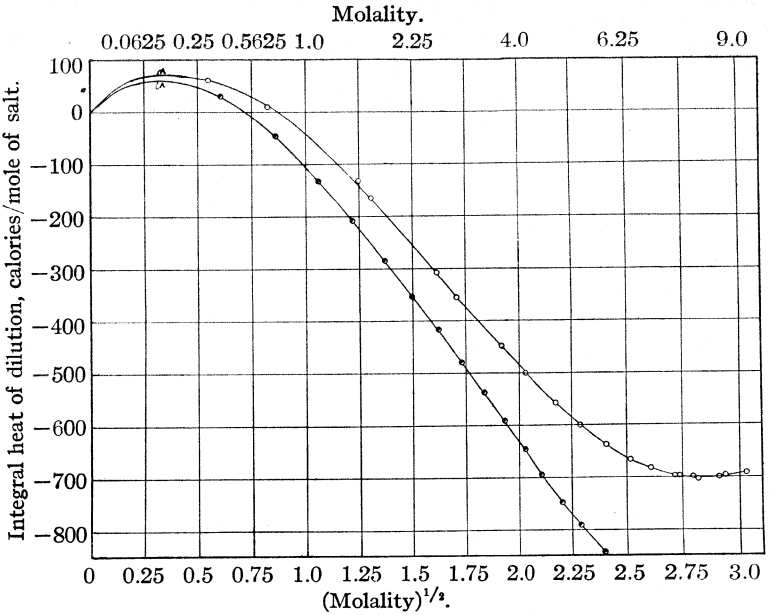


Fig. 1.—Integral heats of dilution at 25°.

of sodium bromide is represented by $\Delta H_{\text{int.}} = -359\, m^{1/2}$; for potassium bromide $\Delta H_{\text{int.}} = -350\, m^{1/2}$. The individual nature of these curves for salts of the same valence type has been discussed before.[6]



○, NaBr; ◐, KBr. Curves to A, these measurements.

Fig. 2.—Integral heats of dilution at 25°.

TABLE II

INTEGRAL HEATS OF DILUTION AT 25°

Concentration moles/1000 g. H_2O	$\Delta H_{\text{int.}}$, calories/mole salt NaBr	KBr	Concentration, moles/1000 g. H_2O	$\Delta H_{\text{int.}}$ calories/mole salt NaBr	KBr
0.0000	0.0	0.0	1.00	39	106
.0001	− 3.5	− 3.5	1.44	116	201
.0004	− 7.0	− 7.0	2.25	256	353
.0016	−14.5	−14.0	3.24	396	521
.0025	−18	−17.6	4.00	484	633
.0064	−29	−28	4.84	566	743
.01	−36	−34	5.68 (satd.)		841
.04	−60	−52.8	5.76	636	
.09	−70.5	−61.3	6.25	664	
.16	−72	−61.5	7.29	695	
.25	−66	−52	7.84	701	
.64	−19.5	23.5	8.41	700	
			9.16 (satd.)	694	

[6] Lange, *Z. Elektrochem.*, **36**, 772 (1930); Lange and Robinson, *Chem. Rev.*, 9 89 (1931).

The integral heat of dilution[7] is related to the relative partial molal heat contents of solute and solvent by $-\Delta H_{\text{int.}} = \bar{L}_2 + n_1\bar{L}_1$, where n_1 moles of water are associated with one mole of salt at a given concentration. Values for $\bar{L}_1$ and $\bar{L}_2$ are most readily obtained from heat of dilution data by the method of Rossini,[7] using the slopes of the curves of Fig. 2. Figure 3 shows a plot of $\bar{L}_1$ and $\bar{L}_2$ for sodium bromide and potassium bromide

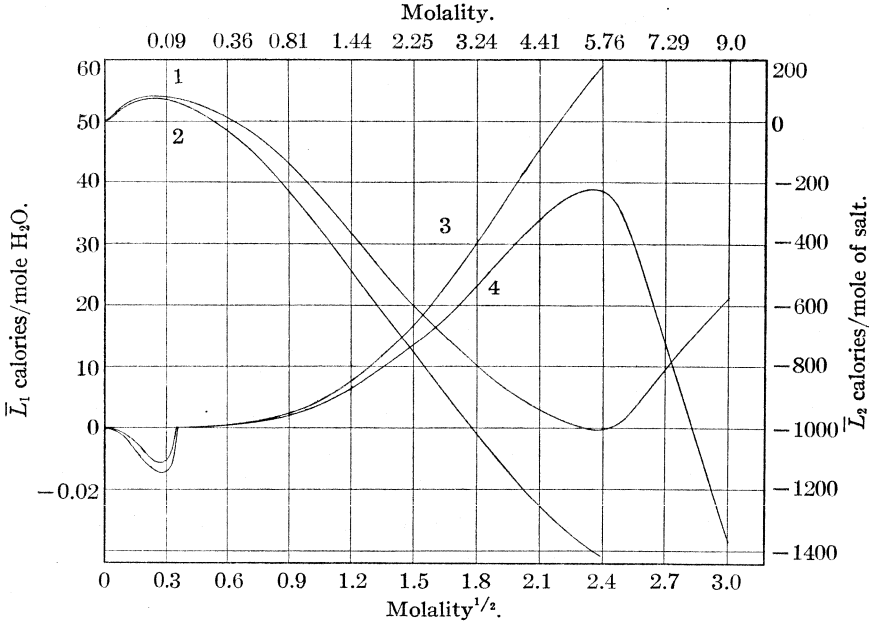


Fig. 3.—Relative partial molal heat contents at 25°. $\bar{L}_1 = \bar{H}_1 - \bar{H}_1°$. $\bar{L}_2 = \bar{H}_2 - \bar{H}_2°$. Curve 1, $\bar{L}_2$ NaBr; Curve 2, $\bar{L}_2$, KBr; Curve 3, $\bar{L}_1$ KBr; Curve 4, $\bar{L}_1$ NaBr.

solutions so obtained and the values of Table III are interpolated from these curves. L_s is the relative molal heat content of the solid salt (referred to the standard state of infinite dilution) and is calculated from the data of Wüst and Lange on integral heats of solution; L_s for sodium bromide is for the anhydrous salt, although the saturated solution at 25° is of course in equilibrium with $NaBr{\cdot}2H_2O$.

Rossini[8] has shown that at 25° up to concentrations of 2.5 M the partial molal specific heats of sodium bromide solutions are represented by $\bar{c}_{p_2} = -24.3 + 20.4\, m^{1/2}$ for the sodium bromide and $\bar{c}_{p_1} = -0.123\, m^{3/2}$ for the water and for potassium bromide solutions $\bar{c}_{p_2} = -29.5 + 16.2\, m^{1/2}$ and $\bar{c}_{p_1} = -0.097\, m^{3/2}$. These values can probably be used up to saturation

[7] This is the negative of the function $\phi_h - \phi_h^\circ$ used by Rossini [*Bur. Stand. J. Res.*, **6**, 791 (1931)] and called by him the relative apparent molal heat content of the solute.

[8] Rossini, *Bur. Stand. J. Res.*, **7**, 47 (1931).

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM BROMIDE AND POTASSIUM BROMIDE SOLUTIONS AT 25°

Concentration, moles/1000 g. H_2O	$\bar{L}_1$[a] calories/mole H_2O NaBr	KBr	$\bar{L}_2$[a] calories/mole salt NaBr	KBr
0.0	0.0	0.0	0.0	0.0
.001	− .0005	− .0004	11	9
.005	− .0016	− .001	38	30
.01	− .0031	− .0019	55	46
.05	− .0132	− .0104	79	71
.1	− .0138	− .0098	76	68
.2	.05	− .08	56	37
.5	.7	1.0	− 32	− 91
1.0	3.0	3.6	− 208	− 311
1.5	6.8	8.2	− 384	− 509
2.0	11.4	13.6	− 540	− 680
2.5	15.7	19.8	− 656	− 825
3.0	20.4	26.5	− 753	− 958
3.5	25.8	33.3	− 834	−1078
4.0	30.6	40.3	− 899	−1183
4.5	34.5	46.4	− 947	−1271
5.0	37.7	52.0	− 983	−1347
5.5	38.9	56.6	−1003	−1394
5.68 (satd.)		58.9		−1414
6.0	37.2		− 994	L_s = −4727
6.5	30.0		− 938	
7.0	20.3		− 858	
7.5	10.0		− 775	
8.0	0.8		− 706	
8.5	− 5.7		− 662	
9.16	−18.5		− 576	
			L_s = 44	

[a] Negative values indicate heat evolved.

concentrations[9] and are useful in conjunction with the values of the relative partial molal heat contents reported here.

The experimental portion of this work was kindly supported by the Notgemeinschaft der Deutschen Wissenschaft, the Kaiser Wilhelm Institute for Physics and the Munich Univeritätsgesellschaft.

Summary

The heats of dilution of aqueous sodium bromide and potassium bromide solutions have been measured at 25° from 0.1 *M* to 0.0002 *M* and extrapolated to infinite dilution. These measurements have been combined with the data of Wüst and Lange, which extend to saturation concentrations, to obtain values for the integral heats of dilution and relative partial molal heat contents of solvent and solute for the entire concentration range.

PITTSBURGH, PENNSYLVANIA

[9] For example see Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

TERNARY SYSTEMS[1]

$CaCl_2$–$Ca(NO_3)_2$–H_2O (25°), $CaCl_2$–$Ca(ClO_3)_2$–H_2O (25°) $SrCl_2$–$Sr(NO_3)_2$–H_2O (25°), KNO_3–$Pb(NO_3)_2$–H_2O (0°)

BY WILLIAM F. EHRET

RECEIVED APRIL 6, 1932 PUBLISHED AUGUST 5, 1932

The chemical literature abounds with references[2] to double and complex salts of the type RX—R′X where R and R′ are two different simple or complex radicals and the common radical, X, is Cl^-, $(CN)^-$, $(NO_2)^-$, Br^-, $(NO_3)^-$, $(SO_4)^=$, etc. Much fewer and more isolated are records of salts of the type RX—RX′. It was with the hope of discovering additional compounds of this type that the present work was begun. The systems chosen for study were selected because of the interest centering in the question of whether complex compounds are formed in solutions of very soluble, highly ionized alkaline earth salts containing anions both of which are strongly negative in character. Recent measurements of migration numbers in similar solutions,[3] but of the type RX + R′X + H_2O, indicate that rather extensive complex ion formation takes place. The study of the system KNO_3–$Pb(NO_3)_2$–H_2O (type RX—R′X) was undertaken for reasons mentioned later in connection with the isotherms.

Experimental Details

The systems at 25° were run in a water thermostat of the Freas type, the temperature being kept constant at 25.0 ± 0.01°. "Non-Sol" glass bottles, containing the salt solutions, were rotated in the thermostat. The temperature of the 0° thermostat was kept constant to ±0.05° by means of felt insulation and an ice–water mixture.

In all the systems the various mixtures of salts and water were made by starting with a bottle containing only one salt and water and in each subsequent run more of the second salt was added to the solution and solid left from the previous run. In the systems $CaCl_2$–$Ca(NO_3)_2$–H_2O and $CaCl_2$–$Ca(ClO_3)_2$–H_2O it was frequently necessary to add the dehydrated salts, since, as will be seen from the isotherms, certain mixtures of the hydrated salts will dissolve completely in their own water of hydration. Two days of rotation in the bath was found by experience to be the minimum length of time necessary to bring the solution and the crystalline residues to equilibrium. In establishing the composition of the new double salt in the system $CaCl_2$–$Ca(NO_3)_2$–H_2O, the bottles containing the saturated solutions in contact with the double salt were kept in the

[1] The greater portion of the experimental work for this paper was conducted at Columbia University and was submitted there in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The remainder of the work was carried out at the Washington Square College of New York University.

[2] Kendall, Crittenden and Miller, THIS JOURNAL, **45**, 993 (1923); Jones and Ota, *Am. Chem. J.*, **22**, 15 (1899); **22**, 110 (1899); Wells, *ibid.*, **26**, 389 (1901) (this paper mentions nearly 500 double halides); Jänecke, *Z. anorg. allgem. Chem.*, **100**, 161 (1917); **100**, 176 (1917).

[3] McBain and Van Rysselberge, THIS JOURNAL, **50**, 3009 (1928).

thermostat for over six months and then re-rotated to ensure equilibrium conditions. It was found by experiment that exactly the same points of equilibrium were reached whether the solutions in contact with the solids were heated to 25° in the bath or whether solutions saturated at a higher temperature were cooled to 25° while turning in the bath. The latter method was found to be quicker, since the dehydrated salts were brought into solution much more readily. In all cases the bottles were re-opened, after they had reached the temperature of the bath, and inoculated with the crystal variety that was thought to be the one which would exist in stable equilibrium with the solution at that temperature.

After the mixtures had come to equilibrium and while still in the bath, samples of the liquid were withdrawn by means of a pipet provided with a folded filter paper at its lower end. When the solutions were viscous, suction, approaching within 2–3 mm. of complete vacuum, was necessary to suck up a sufficient amount of the solution. The latter was immediately deposited in a specific gravity bottle, brought to 25°, and weighed. At the same time about 10–15 g. of the crystals from the same bottle were weighed as quickly as possible to prevent evaporation or absorption of moisture. The weighed samples were diluted in a volumetric flask and aliquots taken for analysis. In the case of the $Pb(NO_3)_2$–KNO_3–H_2O system the samples were not diluted, but were weighed and then dried. The $Pb(NO_3)_2$ and KNO_3 were determined by a method used by Glasstone and Saunders.[4] In the $SrCl_2$–$Sr(NO_3)_2$–H_2O system, strontium was determined as carbonate, and chlorine, volumetrically, by Mohr's method. The nitrate was determined by difference. The method used in the $CaCl_2$–$Ca(NO_3)_2$–H_2O and $CaCl_2$–$Ca(ClO_3)_2$–H_2O systems was as follows: calcium was first precipitated as the oxalate and then determined volumetrically with potassium permanganate. Chlorine was determined volumetrically and the nitrate or chlorate radical by difference. The composition of the solid phases in equilibrium with saturated solutions was determined by the indirect[5] or "residue" method. Results of the analyses are plotted as weight percentages on the triangular diagrams.

The salts used were prepared or purified as follows.

$CaCl_2 \cdot 6H_2O$ was at first obtained by three successive recrystallizations of C. P. $CaCl_2 \cdot 6H_2O$. This method resulted in the loss of about one-quarter to one-half of the material, due to the extreme solubility and the deliquescent character of the crystals. Later the salt was obtained pure by a more economical method due to Morgan[6] in which the salt is melted in its own water of crystallization and then recrystallized. $CaCl_2$ was prepared from the pure hexahydrate by heating in a Freas electrically heated air oven to 110° for several days. A test run, covering a period of nine hours, showed that during this interval no hydrolysis of the $CaCl_2$ had occurred. The salt was kept in a vacuum desiccator. $Ca(NO_3)_2 \cdot 4H_2O$ was prepared by triple recrystallization of C. P. crystals. Later an improved method similar to that given under $CaCl_2 \cdot 6H_2O$ was used. $Ca(NO_3)_2$ was made by heating the purified hydrated salt in an air oven as under $CaCl_2$. During the process of dehydration tufts of anhydrous $Ca(NO_3)_2$ grew up out of the liquefied salt; these were easily removed and the process amounted to a recrystallization as well as a dehydration. The anhydrous salt was tested as was the $CaCl_2$ and then stored in vacuum desiccators. $Ca(ClO_3)_2 \cdot 2H_2O$.—This salt as purchasable is an imported product and the small quantity kept in stock by a large retailer of chemicals was found to be so impure as to make many crystallizations, with consequent losses, necessary. It was thought best to prepare the salt in large enough quantity in the laboratory and for this purpose a new method of preparation was devised. Previous methods,

[4] Glasstone and Saunders, *J. Chem. Soc.*, **123**, 2134 (1923).

[5] Bancroft, *J. Phys. Chem.*, **6**, 179 (1902).

[6] Morgan, THIS JOURNAL, **29**, 1168 (1907).

although they furnished valuable ideas for the new method, were either not considered to yield a pure enough product or were considered too dangerous to work with. The method devised is as follows.

Eight hundred and fifty grams of C. P. barium chlorate crystals is dissolved in two liters of distilled water. About a liter of boiling hot solution of ammonium sulfate, containing enough salt to precipitate almost all the barium, is added, with stirring, to the barium chlorate solution. The remaining barium ion is precipitated with a dilute solution of ammonium carbonate. Complete removal of the barium is tested for with the sulfate test. The precipitated sulfate and carbonate are allowed to settle and the solution of ammonium chlorate removed by filtration. To the solution is added, with stirring, a calcined lime paste containing sufficient chemically pure lime to release all the ammonia and a slight excess. The mixture is then boiled until no more ammonia is driven off. After cooling and filtering, the slight excess of lime is neutralized by means of chloric acid using phenolphthalein as indicator. The resulting solution containing calcium chlorate is boiled down until a drop crystallizes. The crystals obtained by recrystallization contain no impurities except a trace of chloride ion which is not detrimental to the work in hand. $SrCl_2 \cdot 6H_2O$, $Sr(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and KNO_3 were obtained by recrystallizing the so-called chemically pure crystals of the salts from distilled water.

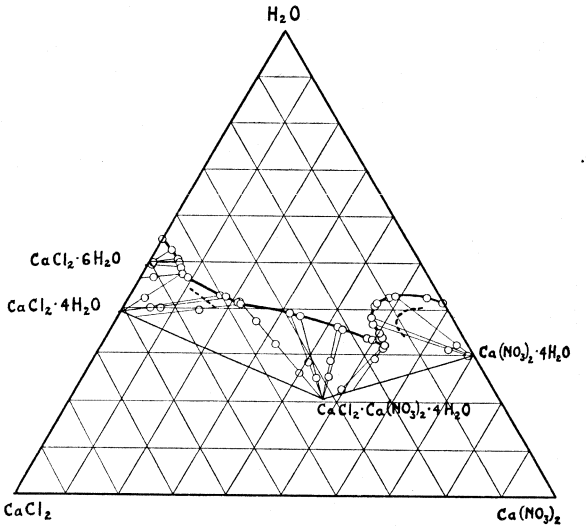


Fig. 1.—The system $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25°.

Experimental Results

The System $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25° (Fig. 1 and Table I).—It will be seen from Fig. 1 that the solid phase in equilibrium with saturated solutions along the first branch of the curve, beginning at the left, is $CaCl_2 \cdot 6H_2O$. Along the next branch, the crystals in equilibrium with the saturated solution are $CaCl_2 \cdot 4H_2O$. They are the alpha modification of the tetrahydrate. At 20.55% $Ca(NO_3)_2$, three phases, namely, double salt, $CaCl_2 \cdot 4H_2O$, and saturated solution, exist together. Then follows the curve

for solutions saturated with double salt ($CaCl_2 \cdot Ca(NO_3)_2 \cdot 4H_2O$) and the right branch of the solubility curve passes through solutions saturated with $Ca(NO_3)_2 \cdot 4H_2O$.

TABLE I

THE SYSTEM $CaCl_2$–$Ca(NO_3)_2$–H_2O AT 25°.

Solution			Residue		
Wt. % $CaCl_2$	Wt. % $Ca(NO_3)_2$	Density	Wt. % $CaCl_2$	Wt. % $Ca(NO_3)_2$	Solid phase
0.00	58.35	1.579			$Ca(NO_3)_2 \cdot 4H_2O$
2.26	55.08	1.581			
7.78	48.88	1.588	2.06	65.59	$Ca(NO_3)_2$ $4H_2O$
8.24	48.93	1.590			
9.19	48.72	1.595			
12.02	46.17	1.616			
12.91	46.45	1.625			
14.57	46.94	1.655	1.20	69.21	$Ca(NO_3)_2 \cdot 4H_2O$
15.06	48.01	1.696	4.22	64.46	$Ca(NO_3)_2$ $4H_2O$
14.73	50.11				
14.45	51.30	1.713			
15.75	50.86	1.790			
15.20	52.21	1.749	18.33	51.91	$Ca(NO_3)_2$ $4H_2O$ + D. S.
16.00	52.29	1.755	27.80	49.12	
16.92	49.28	1.733	23.57	49.02	$Ca(NO_3)_2$ $CaCl_2$ $4H_2O$
17.17	48.37				
21.10	43.02	1.700	26.74	44.18	$Ca(NO_3)_2 \cdot CaCl_2$ $4H_2O$
21.75	41.92	1.692	28.82	45.54	$Ca(NO_3)_2$ $CaCl_2$ $4H_2O$
27.57	34.20	1.660	31.68	43.07	$Ca(NO_3)_2$ $CaCl_2$ $4H_2O$
29.01	31.63	1.651	30.71	40.54	$Ca(NO_3)_2$ $CaCl_2$ $4H_2O$
37.04	22.29	1.623	33.95	39.88	$Ca(NO_3)_2$ $CaCl_2 \cdot 4H_2O$
36.80	21.80	1.624			
36.87	21.15	1.630	34.57	32.77	$Ca(NO_3)_2$ $CaCl_2 \cdot 4H_2O$
37.36	20.94	1.630	36.16	26.17	$Ca(NO_3)_2$ $CaCl_2 \cdot 4H_2O$
37.73	20.55	1.630	46.47	14.69	$CaCl_2 \cdot 4H_2O$ + D. S.
39.75	18.07	1.630	52.75	7.64	$CaCl_2 \cdot 4H_2O$
40.35	16.86	1.619	54.67	5.48	$CaCl_2$ $4H_2O$
43.78	9.03	1.556	54.56	3.01	$CaCl_2 \cdot 4H_2O$
44.98	7.60	1.541	50.47	2.62	$CaCl_2$ $6H_2O$ + $CaCl_2 \cdot 4H_2O$
44.24	6.74	1.523	50.06	0.95	$CaCl_2$ $6H_2O$
44.19	5.77	1.524	50.57	0.00	$CaCl_2$ $6H_2O$
44.14	5.43	1.524	50.17	0.00	$CaCl_2 \cdot 6H_2O$
44.75	2.95	1.474	48.99	1.54	$CaCl_2 \cdot 6H_2O$
44.92	0.00	1.453			$CaCl_2$ $6H_2O$

An interesting property of this system is that crystals of $CaCl_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$, when brought together, often yielded a completely liquid mixture. That this must be so can be seen from Fig. 1. A line joining the points marked $CaCl_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ represents all possible mixtures of the solid salts, and this line would cut the ternary solubility curve in two places and for a considerable space run through the field of

unsaturated solutions. Mixtures of the two salts along this part of the line will liquefy with the formation of unsaturated solutions.

Below the portions of the ternary solubility curve in equilibrium with $CaCl_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ will be found the incomplete solubility curves (broken lines) in this system at 30° as found by Barbaudy.[7] Because of the extreme viscosity of the saturated solutions formed, he obtained no further data. However, the slope of the curves agrees with the slope at 25° and it is therefore very likely that the double salt exists also at 30° and possibly over an even greater range of concentrations.

According to Fig. 1, a solution containing the two salts in approximately the ratio of 60 g. of $Ca(NO_3)_2$ to 40 g. of $CaCl_2$ should upon isothermal evaporation at 25° yield only crystals of the double salt. Furthermore, the double salt, if brought into contact with water at this temperature, will not be decomposed but will continue to dissolve until a saturated solution is formed. The solubility, as estimated from the diagram, is 168 ± 3 g. of anhydrous salt per 100 g. of water.

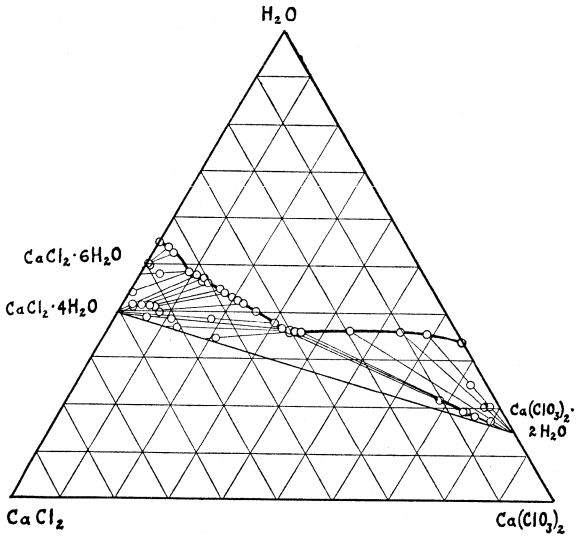


Fig. 2.—The system $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25°.

The System $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25° (Fig. 2 and Table II).—The solubility curve of this system has three branches and shows the absence of any double salt at this temperature. The first branch is in equilibrium with $CaCl_2 \cdot 6H_2O$. The middle branch of the curve represents solutions in equilibrium with $CaCl_2 \cdot 4H_2O$ and the right branch those in equilibrium with $Ca(ClO_3)_2 \cdot 2H_2O$.

[7] Barbaudy, *Rec. trav. chim.*, **42**, 638 (1923).

TABLE II

THE SYSTEM $CaCl_2$–$Ca(ClO_3)_2$–H_2O AT 25°

Solution Wt. % $CaCl_2$	Solution Wt. % $Ca(ClO_3)_2$	Density	Residue Wt. % $CaCl_2$	Residue Wt. % $Ca(ClO_3)_2$	Solid phase
0.00	66.05	1.781			$Ca(ClO_3)_2 \cdot 2H_2O$
5.86	58.65	1.767	1.96	77.89	$Ca(ClO_3)_2 \cdot 2H_2O$
10.31	53.45	1.751	3.08	77.07	$Ca(ClO_3)_2 \cdot 2H_2O$
19.19	44.59	1.731	3.70	79.75	$Ca(ClO_3)_2 \cdot 2H_2O$
28.15	36.02	1.730	7.49	73.56	$Ca(ClO_3)_2 \cdot 2H_2O$
29.21	34.71	1.733	6.77	74.20	$Ca(ClO_3)_2\ 2H_2O$
30.83	33.35	1.733	5.87	76.32	$Ca(ClO_3)_2 \cdot 2H_2O$
30.43	33.01	1.735	10.35	68.20	$Ca(ClO_3)_2 \cdot 2H_2O$
30.56	34.21	1.743	44.65	20.80	$Ca(ClO_3)_2 \cdot 2H_2O$ + $CaCl_2 \cdot 4H_2O$
30.69	32.99	1.742	50.47	12.44	$Ca(ClO_3)_2 \cdot 2H_2O$ + $CaCl_2 \cdot 4H_2O$
30.70	32.81	1.748	50.83	12.78	$Ca(ClO_3)_2 \cdot 2H_2O$ + $CaCl_2 \cdot 4H_2O$
31.49	32.01	1.725	50.86	10.79	$CaCl_2 \cdot 4H_2O$
31.51	30.11	1.718	43.79	18.15	$CaCl_2 \cdot 4H_2O$
34.69	25.20	1.659	53.56	9.44	$CaCl_2 \cdot 4H_2O$
35.59	22.14	1.641	52.40	8.03	$CaCl_2 \cdot 4H_2O$
36.91	21.52	1.625			
36.89	21.02	1.629	55.20	6.09	$CaCl_2 \cdot 4H_2O$
37.75	19.65	1.618	53.99	7.29	$CaCl_2 \cdot 4H_2O$
38.16	17.85	1.606	52.87	6.24	$CaCl_2 \cdot 4H_2O$
38.17	17.69	1.607			
37.92	16.91	1.614	57.59	2.02	$CaCl_2 \cdot 4H_2O$
38.82	16.55	1.603	52.87	6.85	$CaCl_2 \cdot 4H_2O$
40.15	12.29	1.578	56.67	2.18	$CaCl_2 \cdot 4H_2O$
40.53	13.41	1.580	53.91	5.25	$CaCl_2 \cdot 4H_2O$
41.70	12.12	1.565	55.05	3.87	$CaCl_2 \cdot 4H_2O$
41.22	10.70	1.570	56.25	1.81	$CaCl_2 \cdot 4H_2O$
42.82	8.70	1.562	55.19	0.81	$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 6H_2O$
42.41	9.01	1.526	48.18	3.64	$CaCl_2 \cdot 4H_2O$ + $CaCl_2\ 6H_2O$
44.06	3.85	1.480	49.22	1.21	$CaCl_2 \cdot 6H_2O$
43.26	2.36	1.490	49.23	0.63	$CaCl_2 \cdot 6H_2O$
44.92	0.00	1.453			$CaCl_2 \cdot 6H_2O$

The System $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25° (Fig. 3 and Table III).—The solubility curve in this system is again one with three branches, a simple dehydration occurring as in the previous system. No double salt is formed. The left branch of the curve represents solutions in equilibrium with $SrCl_2 \cdot 6H_2O$. The central portion represents solutions in equilibrium with anhydrous $Sr(NO_3)_2$, and the right branch those in equilibrium with $Sr(NO_3)_2 \cdot 4H_2O$.

The System KNO_3–$Pb(NO_3)_2$–H_2O at 0° (Fig. 4 and Table IV).—After the work on the alkaline earth systems was well under way, the system KNO_3–$Pb(NO_3)_2$–H_2O was brought to the attention of the author. Glasstone and Saunders[4] have determined the isotherms at 25, 50 and 100°. Their reason for investigating the system was their belief in the existence of

a complex compound of lead nitrate and potassium nitrate in water solution. Several previous investigations had shown that the solubility of

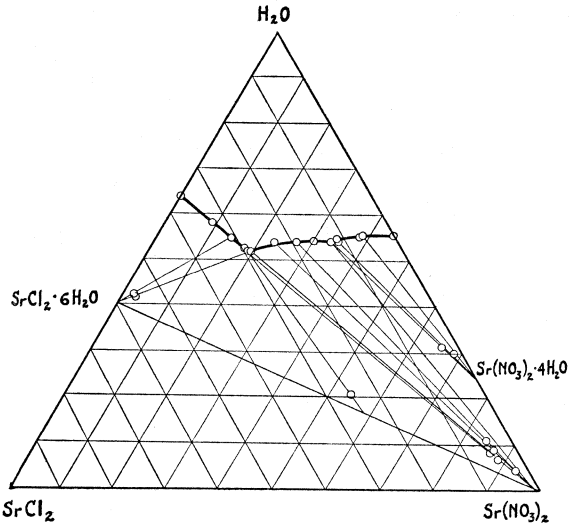


Fig. 3.—The system $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25°.

lead nitrate in water was markedly increased by the addition of potassium nitrate. The increase was attributed to the formation of double molecules

TABLE III

THE SYSTEM $SrCl_2$–$Sr(NO_3)_2$–H_2O AT 25°

Solution			Residue		
Wt. % $Sr(NO_3)_2$	Wt. % $SrCl_2$	Density	Wt. % $Sr(NO_3)_2$	Wt. % $SrCl_2$	Solid phase
44.28	0.00	1.476			$Sr(NO_3)_2 \cdot 4H_2O$
48.69	6.32	1.492			
38.57	5.54	1.488	68.70	1.87	$Sr(NO_3)_2 \cdot 4H_2O$
35.14	10.79	1.508			
34.29	10.87	1.510	65.71	2.97	$Sr(NO_3)_2 \cdot 4H_2O$
33.71	12.11	1.513			$Sr(NO_3)_2$
33.72	12.04	1.513	93.26	2.25	$Sr(NO_3)_2$
30.15	15.10	1.515			
27.25	18.83	1.523	88.45	4.50	$Sr(NO_3)_2$
22.75	23.07	1.537	87.00	4.11	$Sr(NO_3)_2$
19.62	28.45	1.565	86.43	5.06	$Sr(NO_3)_2$
18.91	29.01	1.571			
18.79	28.97	1.568	54.11	24.91	$Sr(NO_3)_2 + SrCl_2 \cdot 6H_2O$
18.07	29.27	1.559			$SrCl_2$ $6H_2O$
18.00	29.23	1.563			
14.10	30.75	1.526	2.99	55.09	$SrCl_2 \cdot 6H_2O$
9.07	32.51	1.483			$SrCl_2 \cdot 6H_2O$
0.00	35.82	1.403			$SrCl_2 \cdot 6H_2O$

in solution, and cryoscopic measurements by Leblanc and Noyes[8] seemed to support this view. They found that mixtures of potassium nitrate and lead nitrate did not depress the freezing point of water as low as would

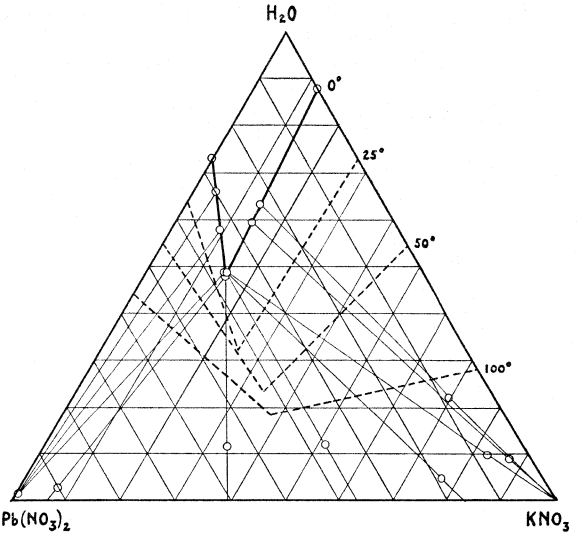


Fig. 4.—The system KNO_3–$Pb(NO_3)_2$–H_2O at 0° (broken curves show results obtained by Glasstone and Saunders).

be expected taking into consideration the common ion effect. Lewis[9] concluded from electromotive force measurements that complexes must be formed upon adding the aforementioned salts to water, for he found a

TABLE IV

THE SYSTEM KNO_3–$Pb(NO_3)_2$–H_2O AT 0°

Solution		Residue		
Wt. % $Pb(NO_3)_2$	Wt. % KNO_3	Wt. % $Pb(NO_3)_2$	Wt. % KNO_3	Solid phase
26.66	0.00			$Pb(NO_3)_2$
29.63	4.15	97.56	0.75	$Pb(NO_3)_2$
32.94	8.95	97.76	0.66	$Pb(NO_3)_2$
37.37	14.20	98.70	0.16	$Pb(NO_3)_2$
37.12	14.74	89.86	7.08	$Pb(NO_3)_2$ + KNO_3
37.14	14.81	54.94	33.29	$Pb(NO_3)_2$ + KNO_3
36.98	15.22	36.25	51.36	$Pb(NO_3)_2$ + KNO_3
37.33	14.66	18.29	76.87	$Pb(NO_3)_2$ + KNO_3
36.27	14.89	7.55	82.87	KNO_3
26.05	14.33	3.92	87.06	KNO_3
22.95	13.67	8.82	69.60	KNO_3
0.00	12.24			KNO_3

[8] Leblanc and Noyes, *Z. physik. Chem.*, **6**, 385 (1890).

[9] Lewis, Dissertation, Breslau, 1908.

diminution of lead ion concentration whenever potassium nitrate was added to a solution of lead nitrate. Although Glasstone and Saunders found no stable double salt in the system at 25, 50 and 100°, the character of their isothermal solubility curves (see dotted curves, Fig. 4) showed distinctly that the solubility influence exerted by potassium nitrate upon lead nitrate was the more decided, the lower the temperature, *i. e.*, the complex, if such exists, is more stable at lower temperatures. Later work, by Glasstone and Riggs,[10] indicated that a double salt, $2KNO_3 \cdot Pb(NO_3)_2$, separated as a solid solution along with $2KNO_3 \cdot Ba(NO_3)_2$ from solutions in the quarternary system KNO_3–$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 25°.

These considerations led the author to believe that a solubility determination at 0° over the whole range of concentrations would establish the existence of an addition compound of the two salts. The system was therefore investigated and the results are given in Table IV and Fig. 4. The solubility curve is composed of only two branches and no double salts are formed. Along the left branch will be found solutions in equilibrium with lead nitrate and along the right branch those in equilibrium with potassium nitrate. It will be noted that the relative increase in solubility of lead nitrate upon addition of potassium nitrate is greatest at 0°. The same may be said about the effect of the presence of lead nitrate upon the solubility of potassium nitrate. Although these are strong indications of the formation of complexes in the solution, a definite compound was not isolable. A number of additional experiments were carried out at −10° with mixtures of lead nitrate, potassium nitrate and water calculated to yield the complex if it exists. No solid phase, different from those already observed at 0°, was found.

The author wishes to take this opportunity to thank Professor James Kendall of the University of Edinburgh for the many valuable suggestions made during the course of the work.

Summary

1. The solubility relations have been determined in the following ternary systems: (I) $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25°, (II) $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25°, (III) $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25°, (IV) KNO_3–$Pb(NO_3)_2$–H_2O at 0°.

2. The existence of a new, stable double salt whose empirical formula is $CaCl_2 \cdot Ca(NO_3)_2 \cdot 4H_2O$ has been established.

3. A new method for the preparation of pure $Ca(ClO_3)_2 \cdot 2H_2O$ is described.

NEW YORK, N. Y.

[10] Glasstone and Riggs, *J. Chem. Soc.*, **127**, 2846 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CONDITIONS FOR PRODUCING TEMPERATURES BELOW 1° ABSOLUTE BY DEMAGNETIZATION OF $Gd_2(SO_4)_3 \cdot 8H_2O$. TEMPERATURE-MAGNETIC FIELD ISENTROPICS

BY W. F. GIAUQUE AND C. W. CLARK

RECEIVED APRIL 8, 1932 PUBLISHED AUGUST 5, 1932

Several years ago one of us[1] devised a method for producing temperatures below those which it has been found possible to obtain by means of liquid helium.

Briefly, the method in its simplest form consists in: (a) magnetizing a suitable paramagnetic substance; (b) absorbing the resulting heat by means of thermal conduction to liquid helium; (c) thermal isolation of the working substance from the helium bath; (d) reversible adiabatic demagnetization with consequent lowering of the temperature.

A few remarks on progress may be of interest here. From the beginning of this problem seven years ago, it has been planned not merely to produce a low temperature but rather to make such temperatures as can be obtained available for experimental work. This has meant the acquisition of apparatus on a scale which has necessitated very slow progress.

The principal requirements are a magnet to produce considerable and very homogeneous fields throughout a large volume and liquefaction cycles of considerable capacity for hydrogen and helium, the liquid hydrogen being required for precooling the helium gas.

A specially built hydrogen compressor with a delivery of 50 cubic feet per minute has been obtained. A very satisfactory hydrogen liquefaction cycle has been constructed. The capacity is about 15 liters of liquid per hour and this can be increased to about 25 liters per hour when a suitable vacuum pump can be obtained for more effective evaporation of the liquid air used for precooling the hydrogen. Storage facilities for 2000 cubic feet of pure hydrogen have been provided.

A helium compressor with a delivery of 25 cubic feet per minute has also been installed and storage facilities for 2000 cubic feet of helium are available. A purification system for removing oil and air or other gases from the helium cycle has been built and it is hoped that the liquefier can be completed in the near future. Acquisition of vacuum pumps permitting recovery of hydrogen evaporated at reduced pressures in the helium cycle and for the reduction of the temperature of liquid helium by reduced pressure is not possible at present.

[1] Giauque, (a) Author's method presented by Professor W. M. Latimer at the meeting of the California Section of the American Chemical Society, April 9 (1926); (b) THIS JOURNAL, **49**, 1864 (1927); (c) *ibid.*, **49**, 1870 (1927). Also see P. Debye, *Ann. phys.*, **81**, 1154 (1926).

An iron-free solenoid magnet with oil-cooled conductors and necessary accessories has been placed in operation. A very homogeneous field is obtained in the central portion of a three-foot cylinder with six inches inside diameter. The magnet has been constructed to take 1000 k. v. a., producing a field of over twenty thousand gauss. At present 100 k. v. a. are available, giving a field of about 8000 gauss. The design of the magnet and helium cycle has been carried out by D. P. MacDougall and one of us. G. F. Nelson has been responsible for mechanical construction of apparatus.

The object of the work reported in this paper was to supply information which would determine the magnetic field requirements and thus provide a sound basis for the design of the magnet referred to above.

Gadolinium sulfate octahydrate is a suitable working substance and a full discussion of its magnetic susceptibility with references to the excellent experimental work of Kamerlingh Onnes, Perrier, Oosterhuis and Woltjer has been given previously.[1b,c] Before the temperature effect produced by the demagnetization of gadolinium sulfate could be determined, it was necessary to know the heat capacity of this substance. It would be preferable to have these data at the temperatures of liquid helium. However, rather than delay until this is possible, it was decided to utilize results at liquid hydrogen temperatures with a Debye heat capacity extrapolation since only approximate results are necessary for our present purpose. Later the heat capacity will be investigated accurately in the liquid helium temperature range. Since no previous measurements have been made on the heat capacity of rare earth compounds at low temperatures it was thought desirable to cover the range to room temperature.

Purity of the Gadolinium Sulfate.—The gadolinium sulfate was obtained from the Welsbach Company, Gloucester, New Jersey, and the analysis furnished by them was Gd 98.5%, Sa 0.5%, Tb 1.0%. These impurities are sufficiently like gadolinium as to introduce a negligible error. A difference of several per cent. in the respective heat capacities would introduce an error of only a few hundredths of one per cent. The average atomic weight of the mixture is but 0.02% lower than that of gadolinium, so the difference may be neglected; 275.804 g. or 0.36926 mole was used in the measurements, the molecular weight of $Gd_2(SO_4)_3 \cdot 8H_2O$ being taken as 746.90.

Heat Capacity Measurements.—The apparatus and calorimetric method were similar to those used in many of the previous low temperature investigations[2] in this Laboratory.

The calorimeter was of copper on which was wound a gold resistance thermometer-heater. The resistance was 365 ohms at 290°K. with a

[2] (a) Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923); (b) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

dR/dT of about 1 ohm per degree from 40 to 290°K. Twelve radial vanes improved the distribution of heat, which was also facilitated by helium gas in the spaces between the gadolinium sulfate crystals. A massive electrically-heated hollow cylinder constructed of copper and lead surrounded the calorimeter and provided a practically constant temperature environment during measurements. The apparatus was enclosed in an evacuated container.

The resistance thermometer was calibrated by means of the standard copper–constantan thermocouple number 16 which was compared with the hydrogen gas thermometer by Giauque, Buffington and Schulze.[3] The thermocouple was attached to the calorimeter during the heat capacity measurements. All low temperatures were produced by liquid air or by liquid hydrogen. The results are given in Table I.

TABLE I

HEAT CAPACITY OF 1/2 MOLE $Gd_2(SO_4)_3 \cdot 8H_2O$ (M. W., 746.90)

$T_{av.}$°K.	ΔT	C_p/1/2 mole in cal./deg.	$T_{av.}$°K.	ΔT	C_p/1/2 mole in cal./deg.
15.42	2.595	1.159	149.59	4.572	42.00
16.55	4.269	1.469	153.73	4.618	43.10
17.64	1.935	1.735	158.63	5.118	44.10
20.23	3.394	2.387	163.73	4.950	45.20
23.60	3.630	3.208	168.88	5.195	46.41
27.25	3.512	4.243	174.31	5.468	47.40
31.56	4.509	5.961	179.78	5.186	48.69
36.02	4.095	7.423	184.94	4.975	49.66
42.67	4.177	9.939	190.12	5.186	50.86
46.93	4.074	11.61	195.30	4.918	52.52
51.26	4.441	13.28	200.20	4.789	52.61
56.15	5.277	15.19	205.23	5.046	53.85
61.82	5.836	17.59	210.35	4.865	54.64
67.55	5.574	19.24	215.35	4.870	54.82
73.22	5.728	21.31	220.36	4.596	55.67
81.28	4.871	23.44	226.97	4.156	57.92
86.12	4.802	25.35	231.89	4.864	58.60
90.76	4.474	26.67	236.92	4.723	59.14
95.33	4.568	28.26	241.95	4.675	61.02
100.17	5.112	29.25	247.00	4.808	61.35
104.88	4.672	30.87	252.13	5.087	62.27
109.46	4.417	32.13	257.34	4.893	63.73
113.98	4.576	33.29	262.46	4.773	63.87
118.64	4.698	34.55	267.56	4.670	64.86
123.19	4.363	35.80	272.62	4.530	66.71
128.47	5.158	37.01	277.82	5.315	66.20
133.69	5.255	38.36	283.25	5.156	66.46
139.06	5.349	39.59	288.86	5.353	68.04
144.53	5.409	41.08			

[3] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

The data are not as accurate as the various low temperature calorimetric investigations made with similar apparatus in this Laboratory within recent years. During the course of the measurements it was found that the thermometer-heater wound on the exterior of the cylindrical calorimeter had an unusually large thermal head with respect to the calorimeter. This greatly increased the usually small correction for radiation to the protective cylinder during heat input and also made it somewhat difficult to obtain equilibrium for the temperature measurements. Following the completion of the measurements the calorimeter was destroyed in order to learn the reason for the difficulty. It was found that the lacquer used on the closely wound thermometer-heater had not adhered to the calorimeter as in previous cases. However, the experimental results are sufficiently accurate and a smooth curve through the points is believed to represent the heat capacity to about 1% at 250°K. and about 0.5% at 100°K.

Since the completion of these measurements, S. Freed[4] has carried out a magnetic investigation on the electronic levels existing in $Sa_2(SO_4)_3 \cdot 8H_2O$. In this connection he has desired to compare the heat capacities of gadolinium and samarium sulfates. We have suggested that the accuracy required in this matter makes it desirable to have the present measurements repeated. We have accordingly given the gadolinium sulfate to Dr. J. E. Ahlberg, who is collaborating with Dr. Freed in this investigation, which should lead to results of increased accuracy. Moreover, for the purposes of comparison some accuracy is gained by measuring both substances in the same calorimeter.

The Entropy of Gadolinium Sulfate Octahydrate at Low Temperatures.—At the temperatures of liquid hydrogen the heat capacity has decreased to such an extent that it seems plausible that the degrees of freedom ordinarily assumed to be represented by the Einstein function are not appreciably active. It is further assumed that the remaining vibrational heat capacity can be represented by the Debye equation. Error resulting from this will be in such a direction as to make the conditions for producing low temperatures more favorable than calculations based on these assumptions will indicate.

Adopting a $\beta\nu = 110$ for $^1/_2$ mole of gadolinium sulfate, the Nernst–Lindemann limiting expression for the Debye equation gives

$$C = \frac{12}{5}\frac{\pi^4 R}{(\beta\nu)^3} T^3 = 3.5 \times 10^{-4}\, T^3 \qquad (1)$$

The arbitrariness in selecting $^1/_2$ mole for determining $\beta\nu$ is of little consequence near the T^3 region. The Debye entropy for the T^3 region is given by

$$S_v = \frac{1}{3}\frac{12\pi^4 R}{5(\beta\nu)^3} T^3 = \frac{3.5 \times 10^{-4}}{3} T^3 \qquad (2)$$

[4] Freed, THIS JOURNAL, **52**, 2702 (1930).

The entropy due to the distribution of the gadolinium ions in the eight states associated with the seven additively coupled electron spins of this ion has been previously considered.[1c]

The expression for the decrease in entropy which accompanies the application of a magnetic field is given by

$$\Delta S_{\mathfrak{H}=0}^{\mathfrak{H}} = R\left[\ln \sum \cosh \frac{gjM\mathfrak{H}\cos\theta}{RT} - \ln 4 - \frac{gjM\mathfrak{H}}{RT}\frac{\sum \cos\theta \sinh \frac{gjM\mathfrak{H}\cos\theta}{RT}}{\sum \cosh \frac{gjM\mathfrak{H}\cos\theta}{RT}} + 0\right] \quad (3)$$

Since the gadolinium ion is an ^8S state, $g = 2$ is the ratio of magnetic to mechanical moment. $j = S = 7 \times {}^1/_2$, the total momentum. M is the molal unit Bohr magneton value. $M = 5567$ ergs/gauss. The summations require four values of $\cos\theta$, namely, 1, ${}^5/_7$, ${}^3/_7$ and ${}^1/_7$. The negative values ordinarily used in addition to these are included by the use of hyperbolic functions.

The above expression assumes that the eight spatial orientations of the magnetic moment are equally probable in the absence of a magnetic field. This cannot be quite true but the magnetic susceptibility data extending to 1.3°K. indicate that the states differ but little in energy.[1c] Further magnetic susceptibility measurements and heat capacity determinations near 1°K. are needed to increase our information concerning the separation of the octet levels. However, the most promising method of obtaining this information appears to be the study of absorption spectra of the solid.

The measurements of Freed and Spedding[5] and more recent work by Spedding[6] and by Spedding and Nutting[7] include observations on $GdCl_3 \cdot 6H_2O$ which has the same crystal structure and very nearly the same absorption spectrum as $Gd_2(SO_4)_3 \cdot 8H_2O$. It would be expected that the two substances have quite similar characteristics. Dr. Spedding informs us that preliminary results indicate disturbances in the ideal separation of the Zeeman components amounting to two or three-tenths of a reciprocal centimeter. Energies of this magnitude become of importance below 1°K. Spedding and Nutting[7] have recently pointed out that the hexagonal crystals $Gd(BrO_3)_3 \cdot 9H_2O$ and $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$ have energy levels which are affected by the crystal forces only to about one-half the extent of the monoclinic crystals $Gd_2(SO_4)_3 \cdot 8H_2O$, $GdCl_3 \cdot 6H_2O$ and $GdBr_3 \cdot 6H_2O$. It is evident that the greater symmetry will produce conditions favorable to maximum magnetic cooling effect. Moreover, it is well known from the many investigations of Kamerlingh Onnes and his collaborators that greater dilution of the paramagnetic atoms by diamagnetic ones permits an increased perfection of magnetic behavior. For these reasons it appears

[5] Freed and Spedding, THIS JOURNAL, **52**, 3747 (1930).

[6] Spedding, *Phys. Rev.*, **38**, 2080 (1931).

[7] Spedding and Nutting, *ibid.*, **38**, 2294 (1931).

that $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, the magnetic susceptibility of which has been investigated to low temperatures by Jackson and Kamerlingh Onnes,[8] will prove superior to $Gd_2(SO_4)_3 \cdot 8H_2O$ as a working substance. It is also evident that best results will eventually be obtained by placing the crystal axis in proper relationship with the magnetic field.

For our present purposes which are purely for determining the order of magnitude in connection with the design of apparatus it will be possible to neglect the effect of the splitting of the energy levels mentioned above. However, as a result of the ideal conditions assumed, the calculated reduction in temperature for a given change in field is greater than will be found experimentally. In fact it may be shown that effects of the order of magnitude found in $Gd_2(SO_4)_3 \cdot 8H_2O$ by Spedding will produce a considerable effect below 1°K. and an appreciable effect extending to several degrees absolute. Nevertheless the figures to be presented in Table IV show the order of magnitude of the ideal limit for a magnetic cooling process utilizing a gadolinium compound. It is possible that a well-diluted crystal with cubic symmetry may make a reasonably close approach to such a limit even below 1°K.

Another consideration that may be of importance is the perfection of the crystals used. Dr. Spedding states that strained crystals give absorption lines which have been broadened to an extent that may lead to an appreciable effect on the magnetic and thermal properties at one or two degrees absolute.

The calculations were made in the following manner. The total entropy, excluding the effect of nuclear spin, and at zero field strength, was taken as $S_T = R \ln 8 + (3.5/3) \times 10^{-4} T^3$. Let ΔS_M be the change (reduction) in entropy caused by the application of the field $\mathfrak{H}$ at temperature T. Then the total entropy for a given situation is

$$S_{T,\mathfrak{H}} = R \ln 8 + \Delta S_M + \frac{3.5 \times 10^{-4}}{3} T^3$$

This must remain constant during a reversible adiabatic change.

Values of ΔS_M were calculated from equation 3 and represented on a large graph. The calculated values have been given in Table II as a function of $(gjM/R) \cdot (\mathfrak{H}/T)$. Table II is for the most part a repetition of the similar values given previously.[1c] However, a correction of the previous values on the basis of 1 calorie (15°) equals 4.185×10^7 joules instead of the value 4.182×10^7 has been made. The table is included to facilitate appreciation of the relatively large amount of entropy under the control of obtainable magnetic fields compared to the small amount concerned in ordinary vibration.

For comparison several values of the vibrational entropy calculated from the expression $S_V = (3.5 \times 10^{-4}/3)T^3$ are given in Table III.

[8] Jackson and Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, No. 168a.

TABLE II

THEORETICAL ENTROPY OF MAGNETIZATION OF $^1/_2$ $Gd_2(SO_4)_3 \cdot 8H_2O$ AS A FUNCTION OF $gjM\mathfrak{H}/RT$

$4.687 \times 10^{-4}\,\mathfrak{H}/T$ gauss/deg.	$-\Delta S_M$ cal./deg.	$4.687 \times 10^{-4}\,\mathfrak{H}/T$ gauss/deg.	$-\Delta S_M$ cal./deg.
0.1	0.004	2.8	1.673
.2	.017	4.2	2.396
.4	.068	6.3	3.064
.7	.196	7.0	3.220
1.4	.663	∞	4.132
2.1	1.195		

TABLE III

VIBRATIONAL ENTROPY OF $^1/_2$ $Gd_2(SO_4)_3 \cdot 8H_2O$

T, °K.	S, cal./deg.	T, °K.	S, cal./deg.
1	0.000117	6	0.0252
2	.000934	7	.0400
3	.00315	8	.0598
4	.00747	9	.0851
5	.0146	10	.117

For example, when a field of 12,000 gauss is applied at a temperature of 10°K.

$$S = R \ln 8 - 0.1275 + 0.1167 = R \ln 8 - 0.0108$$

Then at 0.5°K.

$$R \ln 8 - 0.0108 = R \ln 8 + \Delta S_M + 0.0000146$$

From this ΔS_M is found to be -0.0108 E. U., which corresponds to a value of $gjM\mathfrak{H}/RT = 0.160$ and $\mathfrak{H} = 171$ gauss.

This means that $Gd_2(SO_4)_3 \cdot 8H_2O$ should cool from 10 to 0.5°K. when the magnetic field is reduced from 12,000 gauss to 171 gauss. As may be seen from Table IV, the particular isentropic which was considered above shows that the temperature will fall from 4 to 0.5°K. when the field is reduced from 1780 gauss to 171 gauss.

The results for a number of isentropics are summarized in Table IV.

TABLE IV

TEMPERATURE-MAGNETIC FIELD ISENTROPICS FOR $Gd_2(SO_4)_3 \cdot H_2O$

Each column represents a line of constant entropy

T, °K.	Gauss						
10	20000	15000	12000	11400	11100	10100	7800
9	17000	12300	9320	8650	8260	7220	4180
8	14300	10100	6990	6320	5960	4860	0
7	12100	8180	5180	4530	4120	2790	
6	10000	6550	3710	3060	2620	0	
5	8130	5160	2590	1920	1430		
4	6410	3960	1780	1060	0		
3	4750	2880	1170	448			
2	10000	3150	1890	709	0		
1	4970	1570	940	342			
0.5	2430	786	470	171			

The possibilities shown by the tabulated data need little comment. As mentioned above, the amount of entropy under the control of the magnetic field is large compared to the amount concerned in vibration. For this reason conditions appear favorable to the production of extremely low temperatures even if several members of the magnetic octet are rendered inactive at such temperatures by energy differences comparable with kT. It is evident that the cooling effect available is not only sufficient for producing very low temperatures in the gadolinium sulfate octahydrate itself, but is also sufficient to cool simultaneously other materials in addition.

Summary

The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ has been measured from 14 to 290°K. Extrapolation of the heat capacity results combined with the entropy of magnetization previously given has been used to determine the conditions for producing temperatures below 1°K. by reversible adiabatic demagnetization of gadolinium sulfate octahydrate.

The magnetic field–temperature isentropics have been tabulated. The data indicate that the demagnetization of gadolinium sulfate at the temperatures of liquid helium not only provides enough cooling effect to produce temperatures considerably below 1° absolute, but that in addition other substances may be cooled by gadolinium sulfate for investigation of their properties.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CONDUCTIVITY OF SOLUTIONS OF GERMANIC OXIDE[1]

BY CHARLES E. GULEZIAN AND JOHN H. MÜLLER

RECEIVED APRIL 12, 1932 PUBLISHED AUGUST 5, 1932

There are known to exist several modifications of germanium dioxide, the physical and chemical properties of which differ very definitely.[2] The ordinary form—the so-called "hydrolyzed" oxide—is soluble in water and is obtained by the hydrolysis of the tetrachloride. When solutions of this modification are evaporated to dryness, ignition of the residue gives varying yields of a very insoluble variety—the amount depending on the conditions under which the evaporation is carried out and on the temperature at which the residue is ignited. Only traces of this insoluble form can be obtained by directly igniting large quantities of the "hydrolyzed" oxide, whereas repeated evaporations and ignitions of the "evaporated" oxide bring about complete conversion of the soluble to the insoluble

[1] From a thesis presented by C. E. Gulezian in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Müller and Blank, THIS JOURNAL, **46**, 2358 (1924).

variety.[3] Finally, a very soluble, transparent and "glassy" form results on quickly cooling melted germanic oxide obtained from any other variety. This form is amorphous and a true glass, as is indicated by the absence of lines in its x-ray spectrograph and the lack of a sharp break in its heating or cooling curves. Recently, R. Schwarz and E. Huf,[4] from a study of the properties of this oxide both in the solid condition and in solution, conclude that there are three true modifications—two crystalline and one amorphous. The "evaporated" oxide, according to their data, is homogeneous and not a separate variety.

This observed allotropy of germanium dioxide should, therefore, be taken into consideration in any study of the solutions of this substance. Roth and O. Schwartz,[5] in their study of the physical properties of this oxide in solution, give the earliest data on its conductivity. Their work, however, covers only solutions of the above-named "hydrolyzed" oxide, for the specific conductivity of which they obtained values showing very wide differences, depending on whether the solution of the oxide was prepared in the hot or cold. Furthermore, their lowest value for the primary dissociation constant of germanic acid, 1.2×10^{-7}, calculated from their conductivity data, is approximately fifty times the value given by Pugh,[6] 2.5×10^{-9}, and obtained from a potentiometric determination of the hydrogen-ion concentration in solutions containing sodium acid germanate. R. Schwarz and Huf,[4] working with solutions of the fused or "glassy" oxide, found 0.5×10^{-7} for this constant, which, though less than the value of Roth and Schwartz, is still about twenty times that of Pugh. The present study was undertaken in order to determine the conductivity of this substance in solution under different conditions with special reference to the influence, if any, of polymorphism on the conductivity, and also to determine the more probable of the above-mentioned values for the dissociation constant of the acid formed when the oxide is dissolved in water.

Preparation of Pure Germanium Dioxide

As will be seen from the experimental data to be given later, solutions of pure germanic oxide have an extremely low conductivity, which makes it imperative that the solid be prepared in such a way that it will be absolutely free of foreign ions capable of contributing to conductance. Considerable difficulty was experienced at first in getting concordant results with what was thought to be very pure oxide. When the sample was re-purified, such difficulties were overcome; and since, in an investigation such as this, the most important single factor affecting the final results seems to be the purity of the material used, considerable information will be given concerning its source and method of purification.

[3] Müller, *Proc. Am. Phil. Assoc.*, [3] **65**, 183 (1926).

[4] Schwarz and Huf, *Z. anorg. allgem. Chem.*, **203**, 188 (1931).

[5] Roth and Schwartz, *Ber.*, **59A**, 338 (1926).

[6] Pugh, *J. Chem. Soc.*, 1994 (1929).

"Hydrolyzed" Germanic Oxide (Lot 1).—The original sample of oxide used in this investigation was obtained from germanite. The mineral was decomposed with nitric acid and the undissolved residue containing germanic oxide, siliceous gangue, etc., heated with concentrated hydrochloric acid, the crude germanium tetrachloride distilling out in the usual manner. The tetrachloride was then redistilled and the product hydrolyzed to oxide—most of which was deposited as the difficultly soluble solid. The acid filtrate from this hydrolytic decomposition was purposely discarded in order to eliminate rapidly most of the arsenic. This yield of solid oxide was then dissolved in water and the remaining traces of arsenic removed by rendering the solution faintly acid and adding hydrogen sulfide. The snow-white disulfide was then precipitated in the filtrate in the presence of 6 *N* sulfuric acid and the solid hydrolyzed to oxide by boiling with water in the absence of air. This residue of oxide was once more converted to chloride and the final transformation to oxide effected by collecting the chloride under ice water and warming. The solid so obtained was washed with cold water and then repeatedly moistened and ignited at 950° until no test for chloride ion was observed on dissolving two gram samples in water.

(Lot 2).—The solutions prepared from Lot 1 and used in all the preliminary experiments were combined and concentrated by slow evaporation to about one liter. The germanium was distilled out as chloride in a current of pure hydrogen chloride and the chloride collected, this time, not under water, but under ice cold, concentrated hydrochloric acid.

The advantages of this method will be discussed fully in a forthcoming contribution by Mr. E. R. Allison of this Laboratory. The lower layer of chloride was then run, drop by drop, from the ice-jacketed separatory funnel in which it had been collected into a large platinum dish containing about 300 cc. of conductivity water heated to 45–50° and kept in constant agitation. No solid oxide separated out at first—even after the addition of about forty grams of chloride. Then the apparently clear dispersion of chloride and water gave way to a very finely divided and heavy precipitate of germanium dioxide. The solid appeared uniform in structure, the absence of cakes or lumps of the oxide being especially noticeable. The precipitated oxide was filtered, washed with cold water and warmed with about 50 cc. of conductivity water. After a second filtration, the residue remaining on the filter was washed until apparently clear of chloride ion. This entire behavior was strikingly different from that observed when the chloride is hydrolyzed according to the usual method of adding it in bulk to water and gradually warming. The small amount of chloride lost by volatilization in the method described is more than compensated for by the improved condition of the oxide obtained, which makes subsequent purification much less difficult. Even though the wash water gave a negative test for chloride ion, large samples of the solid when dissolved in water gave good positive tests. The removal of the final traces of hydrogen chloride was effected only by ignition of the moistened oxide at temperatures above 900°. Only about five or six such ignitions are required when the oxide is obtained in the manner described, whereas at least twice as many are necessary when it is prepared by the other method.

(Lot 3).—A third yield of "hydrolyzed" oxide was prepared indirectly through the sulfide. Pure oxide solutions obtained from Lot 2 were made 6 *N* with hydrochloric acid and the sulfide precipitated with hydrogen sulfide obtained from liquid hydrogen sulfide. The filtered disulfide was washed with 6 *N* acid saturated with hydrogen sulfide, then with hydrogen sulfide water and finally with conductivity water. After drying in a desiccator over soda lime for three days, the sulfide was changed to chloride by Winkler's method[7] with the use of pure mercuric chloride. The distillate collected in a cooled receiver was redistilled and the portion boiling below 84° collected, as before,

[7] Winkler, *J. prakt. Chem.*, **36**, 188 (1887).

under pure concentrated hydrochloric acid. The subsequent transformation to oxide and purification of the latter were carried out exactly as in the preparation of Lot 2.

"Glassy" Germanic Oxide.—"Hydrolyzed" oxide from Lot 2 or 3 was placed in a platinum boat and the temperature raised to about 1250° in an electrically heated platinum resistance furnace. After removal from the furnace and quick cooling in the air, the sample was dissolved, without grinding, in conductivity water.

Germanic Oxide from the Sulfide.—About six grams of "hydrolyzed" oxide was dissolved in conductivity water and precipitated as sulfide from 6 *N* sulfuric acid solution. After thorough washing of the sulfide—as previously indicated—until visible peptization occurred, it was transformed into oxide in a quartz flask by the hydrolytic method.[8] Superheated steam was passed through the liquid until the escaping vapors gave no test for hydrogen sulfide. Evaporation of the liquid to dryness in a platinum dish and ignition at 950° for eight hours gave a residue of oxide, 2-g. samples of which in conductivity water showed no visible test for sulfate ion.

Germanic Oxide Crystallized at 1050°.—"Hydrolyzed" oxide was melted as above, but instead of removing and cooling the melt quickly, the sample was cooled slowly in the furnace to 1050 ± 5°, and kept at this temperature for about five hours. When removed and broken up, observation of the solid under an ordinary microscope indicated the presence of a mass of large well-formed crystals. As the oxide obtained in this way dissolved much more slowly than the other samples, it was finely powdered in a quartz mortar before addition to water.

Insoluble Germanic Oxide.—The material was a 10-g. sample prepared in a previous investigation.[3] It was repeatedly treated with boiling conductivity water in order to remove all traces of soluble matter—the boiling being carried out in a quartz flask. A redetermination of the solubility of the material thus obtained showed that 2.3 milligrams dissolved per liter at 25°.

Conductivity Measurements

Apparatus and Reagents.—The usual Kohlrausch set-up was used with a thousand cycle microphone hummer as the source of alternating current. The slide was a Gray instrument with the scale divided into a thousand divisions. The variable resistance was a Leeds and Northrop instrument accurate to 0.1%—as checked against L. and N. standard resistances. A variable air condenser was placed in parallel with the resistance box to compensate for capacitance in the conductivity cell. All readings, except those on conductivity water, were taken with the end-coils of the slide wire in the circuit, thereby greatly increasing the accuracy of the bridge reading.

The thermostat was maintained at 25.00 ± 0.02°, the temperature being read with a calibrated thermometer.

All glassware was thoroughly cleaned and steamed before use, and all measuring apparatus calibrated. The heating of all germanic oxide solutions used in the measurements was carried out either in platinum dishes or quartz vessels.

The conductivity cell was made of Pyrex glass with the exception of a ground-glass stopper and the supporting tubes through which the electrodes were sealed. The electrodes were about three centimeters in diameter and about four millimeters apart. The cell constant, 0.02564, was checked frequently during the determinations and the change found to be inappreciable.

The potassium chloride was a sample of Kahlbaum's best grade recrystallized from conductivity water and heated to 300° for two to three hours just before use. The solutions necessary for the determination of the cell constant were prepared according to the data given in the "International Critical Tables."[9]

[8] Müller and Eisner, *Ind. Eng. Chem., Anal. Ed.*, **4**, 134 (1932).

[9] "International Critical Tables," Vol. VI, p. 230, Table I.

The specific conductivity of the water used was in all cases below 1.0×10^{-6} mho per cm. The water was kept in well steamed and seasoned Pyrex flasks which were always kept filled with water until immediately before use, all samples of water being used within ten hours after collection.

Preliminary Experiments.—(a) In this and in all the other preliminary experiments, the conductivity measurements were made at 30° with samples of the oxide taken from Lot 1. Solutions of the "hydrolyzed" oxide of the same concentration (2.276 g. per liter) were prepared at 0° and at 100°. The specific conductivity was approximately the same for solutions made at both temperatures—between 6.5 and 8.0×10^{-6} mhos per cm. At the same concentration—but at 18°—Roth and Schwartz[5] obtained a value of about 17×10^{-6} mhos per cm. for the solution prepared in the cold and of about 35×10^{-6} mhos per cm. for that prepared in the hot (the temperatures at which the solutions were prepared not being stated in either case). Our experiments were easily duplicated and indicated that extremes of temperature in the preparation of such solutions had very little, if any, effect on the conductivity. After being kept in Pyrex flasks for several days, the solutions were found to be quite stable, only very slight changes in conductivity being observed.

(b) Samples of a similar solution of "hydrolyzed" oxide were then sealed up in previously cleaned and steamed quartz bulbs of 25-cc. capacity, and heated continuously for seven days in a boiling water-bath. A bulb was removed every twenty-four hours and the conductivity of its contents determined. Throughout the entire period, no changes over 1% were observed. The same experiment was carried out for solutions of the "glassy" form—the original solution in this case being prepared at 0°. Water blanks were also prepared and kept in the same bath throughout the run. After an initial slight increase—equal to that in the case of the water in the blanks—the values observed were constant over a period of five days. Solutions kept thus for four days at temperatures of 0, 30 and 65° also showed a similar stability.

(c) The sample of oxide used in the preparation of all these solutions had been ignited at 950° in order to remove traces of hydrogen chloride. It was thought that, perhaps, on heating, the germanic oxide had undergone some change in its physical condition that was responsible for its low conductivity when placed in solution. Attempts were then made to remove the hydrogen chloride from the hydrolyzed oxide at lower temperatures. The material was repeatedly extracted with boiling conductivity water; it was moistened and ignited at various temperatures up to 700°; superheated steam was passed over it at temperatures up to 500°; it was moistened several times and heated *in vacuo* at 500°; but, no matter what method was used, the residues when dissolved in conductivity water still gave good positive tests for chlorine. All attempts to obtain chloride-free germanic oxide at temperatures much below 900° were then given up. That such a high temperature is required to remove all the hydrogen chloride is quite remarkable. It may be that the last traces leave only with the last traces of water, which Dennis, Tressler and Hance[10] have shown to be completely removed only on heating to 950°. It is, perhaps, due to this fact also that Roth and Schwartz obtained the results which they report, since they state that, in purifying the oxide, the final step consisted in heating to a "dull-red" heat—which is considerably below 900°. R. Schwarz and Huf[11] report more than 0.1% of chlorine in the oxide ignited at 600°, and succeeded in eliminating all the chlorine at 800°.

(d) The conductivity of solutions of the "evaporated" oxide was then studied in order to determine whether it differed from that of the hydrolyzed modification. Solutions of the hydrolyzed oxide were evaporated in electrically heated platinum dishes.

[10] Dennis, Tressler and Hance, THIS JOURNAL, **45**, 2033 (1923)

[11] Ref. 4, p. 196.

The results of four such experiments indicated a drop in specific conductivity from 24 to approximately 7.5×10^{-6} mhos per cm. Enough of this "evaporated" oxide was then obtained to heat one-gram portions to various temperatures in order to change some of it to the insoluble form and then to determine the influence of such heat treatment on the conductivity of the unchanged solid. In each case, the insoluble oxide was rapidly filtered off with suction and the conductivity of the filtrates determined. The concentration of the solutions obtained was found—as in all previous cases—by evaporating accurately measured 50.0-cc. portions to dryness in a small quartz beaker and igniting in the same vessel to constant weight. Table I summarizes the observations made.

TABLE I

THE CONDUCTIVITY OF IGNITED SAMPLES OF "EVAPORATED" GERMANIC OXIDE

Nature of sample	$k \times 10^6$ mhos/cm.	Concn. g./liter	$k \times 10^6$ mhos/cm. (for 4.8 g./liter)
Hydrolyzed oxide	24.54	4.792	24.58
Evaporated oxide	7.94	4.786	7.96
Evaporated oxide (to 380°)	7.72	5.464	6.78
Evaporated oxide (to 700°)	5.13	4.948	4.98
Evaporated oxide (to 850°)	4.67	5.058	4.43
Evaporated oxide (to 1250°)	3.85	4.796	3.85

In the last column are shown values for the specific conductivities of all the solutions at the same concentration—calculated on the assumption that, between such small limits, a straight line relationship exists between concentration and specific conductivity.

Either one of two explanations was thought capable of accounting for these results: (1) the portion of the oxide not transformed to the insoluble variety may be so changed as a result of the increasingly high temperatures to which it is subjected that on subsequent solution it is hydrated in a continually different manner, or (2) there may have been present in the hydrolyzed oxide an impurity removable by evaporation and ignition—the impurity being completely driven out on heating to the melting point (approx. 1100°).

(e) It was then decided to repurify the oxide used. This was done as described above for the preparation of Lot 2 of the hydrolyzed oxide. The evaporations of this especially pure material were carried out in a quartz flask closed to the air and immersed in a thermostat kept at about 60°. The evaporation was aided by passing air through a purifying train containing silver nitrate solution, concentrated sulfuric acid, concentrated sodium hydroxide, solid sodium hydroxide and blowing it across the surface of the evaporating liquid. The air was introduced through quartz tubes sealed into a tightly fitting quartz stopper, while the escaping air and water vapor passed out through a small indentation on the side of the stopper. Under these conditions the changes observed in the specific conductivity when the "evaporated" oxide was redissolved in water were very small—about 2 to 3% of the original values, which, as shown in Table II, were themselves extremely low. Successive evaporations had, likewise, little or no effect on the conductivity.

Final Determinations.—These determinations were made on solutions of the oxide prepared from Lot 2 or 3. They were all obtained by boiling a weighed sample in a quartz flask with conductivity water until a clear solution was formed, cooling the solution to room temperature and determining the specific conductivity at 25°. The concentration was then determined accurately, as described above, on a carefully measured

volume of the solution—the sample being taken at 25°. Table II gives a summary of these observations.

TABLE II

THE SPECIFIC CONDUCTIVITY OF GERMANIC OXIDE AT 25°

	Source of sample	Concn., g./liter	$k \times 10^6$ (mhos/cm.)	$k \times 10^6$ mhos/cm. (for water)
1	Hydrolyzed (Lot 2)	4.720	2.91	0.96
2	Hydrolyzed (Lot 2)	4.720	2.99	.93
3	Hydrolyzed (Lot 3)	4.720	2.74	.92
4	Glassy (Lot 2)	4.658	2.78	.89
5	1050° (Lot 2)	5.520	5.41	1.00
6	From sulfide (Lot 3)	4.845	4.57	0.90

Table III shows the calculated values for the degree of dissociation, the equivalent conductivity and the primary dissociation constant of germanic acid as obtained from each of the observations recorded in Table II.

TABLE III

THE DEGREE OF DISSOCIATION, EQUIVALENT CONDUCTIVITY AND PRIMARY DISSOCIATION CONSTANT OF GERMANIC ACID

	Concn., mole/liter	$k \times 10^6$ mhos/cm.	$k \times 10^6$ mhos/cm. (corr.)	$\alpha \times 10^4$	Λ	$K_1 \times 10^9$
1	0.04513	2.91	2.73	1.59	0.0606	1.14
2	.04513	2.99	2.87	1.67	.0636	1.26
3	.04513	2.74	2.61	1.52	.0578	1.04
4	.04453	2.78	2.65	1.56	.0595	1.09
5	.05277	5.41	5.34	2.66	.101	3.73
6	.04632	4.57	4.50	2.55	.0970	3.00

In the case of each of the above solutions, dilutions were made and the specific conductivities determined at each concentration. The dissociation constants calculated decreased for all the solutions with decreasing concentration and remained fairly constant within the range 0.95 and 1.1×10^{-9}.

The only added electrolyte in all these solutions was the germanic oxide, which in the presence of water forms germanic acid. The specific conductivity of the water used was close to the value 0.85×10^{-6} mho per cm. found by Kendall[12] for "equilibrium water," and therefore we can make the assumption that the entire conductivity of the water was due to carbonic acid. In view of the very low conductivities observed, it is impossible to ignore the mutual effect of the two acids, carbonic and germanic, on their dissociation. A correction must be applied for this effect, and in making the above calculations this correction was determined by the method of Walker and Cormack.[13] Column 3 of the last table gives the corrected value for each of the specific conductivities recorded. The value of Λ_∞ for germanic acid which is needed in these calculations was

[12] Kendall, THIS JOURNAL, **38**, 1480 (1916).

[13] Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

taken as 381.2, and was obtained by adding the mobilities of the hydrogen ion and the bigermanate ion. The value for the hydrogen ion, 349.9 at 25°, was taken from the "International Critical Tables,"[9] while the value for the bigermanate ion, 31.3, was obtained from measurements on the conductivity of sodium bigermanate—the data for which are given in the following paper. The dissociation constant of carbonic acid at this temperature was taken as 3.5×10^{-7}, and the concentration of carbon dioxide in equilibrium water at this temperature as 1.4×10^{-5} mols per liter.[12]

In order to complete the study of the conductivity of solutions of the allotropes of germanic oxide, several experiments were carried out with the insoluble variety—obtained as already described. The purified sample was boiled repeatedly with conductivity water in a quartz flask. The specific conductivity of solutions thus boiled in the presence of the solid for varying lengths of time up to four hours showed no appreciable increase over the value for the conductivity water used in preparing the solutions. This is to be expected in view of the very low solubility of the α modification and the extremely low conductivity of even saturated solutions of the soluble varieties.

Discussion

The results obtained indicate that solutions of germanic oxide are quite stable, at least over a period of a week at the concentrations studied. Extremes of temperature do not seem to bring about any changes in the fundamental equilibria set up when the oxide is first dissolved in water, no matter whether an amorphous or crystalline variety is involved in the equilibria. Furthermore, the fact that at similar concentrations, solutions of the "evaporated" and "hydrolyzed" oxides have similar conductivities lends support to the conclusion of R. Schwarz and Huf that they are not distinct modifications, in spite of the observed differences in density and in their behavior on ignition. On the other hand, it is difficult to explain the fact that solutions of the "glassy" and "hydrolyzed" forms give practically the same conductivity—since it has been shown[3,4] from x-ray spectrographic data that the one is amorphous and the other crystalline. It may be that the low values for these two varieties are due entirely or in large part to electrically charged colloidal particles, whereas, in the cases of the oxide obtained from the sulfide and that crystallized at 1050°, the amount of colloid in solution is relatively small. The higher conductivities observed in the solutions of the latter two samples would then be due almost entirely to dissociated germanic acid. In other words, all solutions of germanic oxide—no matter from what source—contain both molecularly and colloidally dispersed material with the one or the other in greater amount depending on the source and manner of preparing the solutions. This would explain the small differences in conductivity observed for the

different samples and would be in agreement with the conclusion to which Schwarz and Huf arrived on the basis of their data concerning anomalies in the solubility of the oxide.

In any event, the very low conductivities observed in all the cases indicate a very high degree of purity for all the samples, and should serve to place a definite upper limit for the value to be assigned to the primary dissociation constant of germanic acid. Both the high and low values agree very well with the average value of Pugh, *i. e.*, 2.5×10^{-9}; and when it is considered that Pugh's average was obtained from the three values 1.75, 3.2 and 2.1×10^{-9}, the agreement of our values with his seems to be quite satisfactory. However, in view of the very low conductivities measured, it was thought advisable to determine the value of the constant by other and independent methods. These are discussed in a subsequent paper.

Summary

1. The importance of exceptionally pure germanic oxide in conductivity work has been discussed and a description given of the method used to obtain such material.

2. The conductivity of solutions of the oxide from various sources has been measured and the values in all cases found to be much lower than those already in the literature.

3. In contrast to the work of Roth and O. Schwartz, the conductivity of these solutions was found to be practically unaffected by changes in temperature—either during their preparation or after.

4. Small differences in conductivity of solutions of the several varieties were observed and the possible cause for such differences discussed.

5. The dissociation constant of germanic acid was calculated from the conductivity data obtained, and found, at different concentrations, to lie between 1.0 and 3.0×10^{-9}. These values were in close agreement with those of Pugh.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CONDUCTIVITY AND DEGREE OF HYDROLYSIS OF SODIUM BIGERMANATE AND THE PRIMARY DISSOCIATION CONSTANT OF GERMANIC ACID[1]

BY CHARLES E. GULEZIAN AND JOHN H. MÜLLER

RECEIVED APRIL 12, 1932 PUBLISHED AUGUST 5, 1932

The values obtained by the present authors for the conductivity of solutions of germanic oxide of a high degree of purity[2] tend to show that the probable value for the dissociation constant of germanic acid is approximately 1.0×10^{-9}, a value which is far removed from the values 1.2×10^{-7} and 0.5×10^{-7} obtained by Roth and O. Schwartz[3] and R. Schwarz and Huf[4] from similar conductivity measurements. Pugh,[5] whose value for the constant, 2.5×10^{-9}, is in good agreement with our own, attributes the very high value of Roth and Schwartz to the low grade of conductivity water used in their investigation. The specific conductivity of their water was $1.5\text{–}1.7 \times 10^{-6}$ mhos per cm. at 18°, while that of the water used by Schwarz and Huf was $1.8\text{–}2.0 \times 10^{-6}$ mhos per cm. at 20°; but, even though these values are much higher than that desirable for accurate measurements at these temperatures, they do not, alone, seem to be a sufficient explanation of the very wide discrepancy. The low conductivities found by us cannot be ascribed to colloidal dispersion because samples of the oxide which were definitely crystalline gave similar results. Furthermore, no matter from what source the germanic oxide was obtained, the results were always of the same order of magnitude. It seems, therefore, that either the results of other authors are subject to correction or that there exists in our own observations an undetected source of error of considerable magnitude. To remove the doubt that thus exists concerning the value for this constant, it was determined by two other methods, one conductimetric and the other colorimetric.

Outline of Conductimetric Method.—In order to secure some information concerning the behavior of germanic oxide in solution, conductimetric titrations were carried out. The titrations were performed in a closed conductivity cell, the air in which had been passed into it after purification through a line containing silver nitrate, concentrated sulfuric acid and solid sodium hydroxide. The carbonate-free caustic soda was prepared by

[1] From a thesis presented by C. E. Gulezian in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Gulezian and Müller, THIS JOURNAL, **54**, 3142 (1932).

[3] Roth and Schwartz, *Ber.*, **A59**, 338 (1926).

[4] Schwarz and Huf, *Z. anorg. allgem. Chem.*, **203**, 188 (1931).

[5] Pugh, *J. Chem. Soc.*, 1994 (1929).

Cornog's method.[6] Curves for several titrations are shown in Fig. 1. Curve A shows the results obtained when 25.0 cc. of 0.04453 *M* germanic oxide solution was titrated with 0.09287 *M* sodium hydroxide; curve B is for the titration of 25.0 cc. of 0.04632 *M* germanic oxide with the same caustic solution, while curve C gives the changes in specific conductivity when 100.0 cc. of 0.004453 *M* sodium hydroxide was titrated with 0.04453 *M* germanic oxide solution. In all these and similar cases, a definite break was obtained at a point corresponding to one equivalent of each substance.

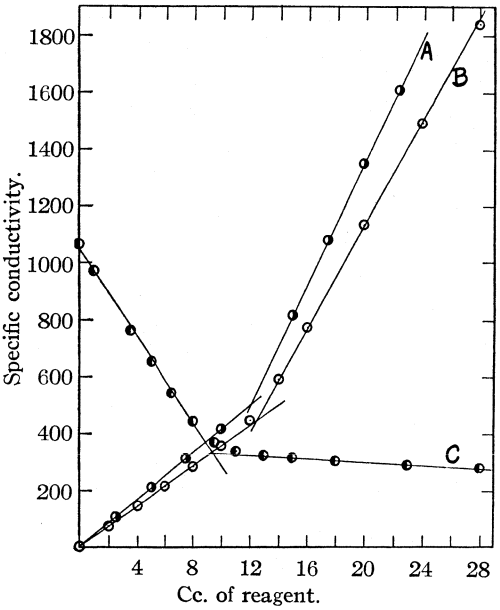


Fig. 1.—The conductimetric titration of germanic acid.

The further addition of sodium hydroxide produced no change in the direction of the curve irrespective of the nature or source of the oxide in solution. Germanic acid, therefore, can behave toward sodium hydroxide as a monobasic acid with the formation of the salt sodium acid germanate (analogous to sodium bicarbonate), evidence for the existence of which has already been given by Pugh. Pugh has also shown that the salt sodium metagermanate, Na_2GeO_3, is hydrolyzed to an extent of 95% or more at concentrations approximately equal to those in our solutions, so that the addition of sodium hydroxide to sodium bigermanate produces no appreciable formation of the normal meta salt. Obviously, accurate measurements of the concentration of germanic acid by conductimetric titrations is impossible due to the occurrence of considerable hydrolysis of the acid salt at the equivalent point—the evidence for this being especially noticeable in Curve C, Fig. 1; but the extent of this hydrolysis can be measured conductimetrically and from the degree of hydrolysis of the salt the dissociation constant of the parent acid can easily be calculated.

The conductimetric method for the determination of the degree of hydrolysis of a salt was originally described by Walker[7] for salts of weak bases. Bredig[8] also applied the method to the determination of the dis-

[6] Cornog, THIS JOURNAL, **43**, 2573 (1921).

[7] Walker, *Z. physik. Chem.*, **4**, 319 (1889).

[8] Bredig, *ibid.*, **13**, 321 (1894).

sociation constants of a number of weak organic bases; while, since then, it has been used to determine the degrees of hydrolysis of salts of weak acids as well as of weak bases. Examples of the application of the method for salts of weak acids are obtained in the work on cacodylic acid,[9] acetic acid,[10] cyanamide[11] and on certain oximes.[12]

In the present case, we have the reaction

$$NaHGeO_3 + H_2O \longrightarrow NaOH + H_2GeO_3$$

taking place in a water solution of this salt. Direct measurement of the conductivity of the salt is, therefore, a measurement of the combined conductivity of the unhydrolyzed salt and of the sodium hydroxide formed. The conductivity of the free acid formed—exceedingly small as it is, even when present in water by itself at much higher concentrations—is here negligible, because of the very large excess of bigermanate ions from the salt. If, now, a buffer solution is formed having a considerable quantity of germanic acid present, hydrolysis of the salt can be prevented almost completely. The acid, again, will not contribute to the conductance of the solution, while complete dissociation of the salt can still be assumed. Measurement of the conductivity of such a solution will give a much more accurate value for the equivalent conductivity of the unhydrolyzed salt. From a knowledge of the equivalent conductivities in the two cases, it is possible to calculate the degree of hydrolysis from the expression.

$$\Lambda = x\Lambda'' + (1 - x)\Lambda'$$

where x is the degree of hydrolysis, and Λ, Λ' and Λ'' are the equivalent conductivities, at the same concentrations, of the hydrolyzed salt, the unhydrolyzed salt and sodium hydroxide, respectively. The value, Λ'', for the sodium hydroxide used at any concentration is assumed to be that which would be obtained if the salt were completely hydrolyzed.

Experimental

The salt, sodium bigermanate, has never been isolated. Attempts to do so proved unsuccessful. It was, therefore, prepared in solution by adding exactly equivalent amounts of carbonate-free sodium hydroxide to known amounts of germanic oxide in solution. The figures in Table I show the method of preparation and composition of the various solutions used.

Twenty-five cubic centimeter portions of each of these solutions were transferred to the conductivity cell, dilutions made and the specific conductivity determined at each dilution. The apparatus was the same

[9] Zawidski, *Ber.*, **36**, 3325 (1903).

[10] Noyes, Kato and Sosman, THIS JOURNAL, **32**, 159 (1910).

[11] Kameyama, *Trans. Am. Electrochem. Soc.*, **40**, 131 (1921).

[12] Brady and Goldstein, *J. Chem. Soc.*, 1918 (1926).

TABLE I

THE PREPARATION OF SODIUM BIGERMANATE SOLUTIONS

Solution	GeO_2, solution, cc.	Concn. GeO_2, mole/liter	NaOH 0.09287 M, cc.	Diluted to	Acid/salt ratio
(1)	100.0	0.04513	48.59	250.0	(Salt alone)
(2)	200.0	.04585	49.37	250.0	1.0
(3)	75.0	.05790	15.59	100.0	2.0
(4)	75.0	.05790	11.69	100.0	3.0

as that described in a previous paper.[2] Tables II, III, IV and V show the observations made on each of the solutions indicated in Table I. At the bottom of each table is included the specific conductivity of the water used in each case.

TABLE II

SOLUTION (1)

$\sqrt{c}$	$k \times 10^6$	Λ
0.1344	1293.7	77.36
.0950	691.1	81.66
.07757	474.8	84.49
.06718	361.4	86.37
.05485	244.5	89.60
.04751	183.2	92.03
.03880	121.7	95.55

k (H_2O) = 0.90×10^{-6}

TABLE III

SOLUTION (2)

$\sqrt{c}$	$k \times 10^6$	Λ'
0.1354	1323.2	72.15
.09576	698.4	76.16
.06771	359.6	78.43
.03789	183.8	80.16
.03387	94.81	82.66
.02395	49.09	85.60
.01694	25.52	88.98

k (H_2O) = 0.90×10^{-6}

TABLE IV

SOLUTION (3)

$\sqrt{c}$	$k \times 10^6$	Λ'
0.1203	1060.5	73.24
.08509	557.3	76.98
.06948	372.8	77.23
.06015	281.1	77.66
.04912	189.8	78.66
.03805	115.7	79.91
.03216	83.55	80.80

k (H_2O) = 0.81×10^{-6}

TABLE V

SOLUTION (4)

$\sqrt{c}$	$k \times 10^6$	Λ'
0.1042	827.0	76.15
.07369	428.3	78.88
.06015	283.4	78.29
.05211	212.8	78.38
.04254	143.4	79.24
.03295	87.23	80.32
.02785	62.81	80.97

k (H_2O) = 0.97×10^{-6}

The Mobility of the Bigermanate Ion.—When plotted against $\sqrt{c}$, the values for the equivalent conductivities for the salt in these four solutions give the results shown in Fig. 2. The points on curve A are for solution (1)—of the hydrolyzed salt. They fall on a smooth curve which rises very rapidly with dilution, indicating increasingly larger amounts of hydrolysis with decreasing concentration. The curve for the 1:1 buffer—curve C in the figure—shows that, in such a solution, hydrolysis is not completely repressed, since it becomes quite appreciable at low concentrations. Curve B is drawn through the points corresponding to the 3:1 buffer (Table V). The points for the 2:1 buffer, as shown, lie sufficiently close to this curve to warrant the conclusion that, in the case of the 3:1 buffer,

hydrolysis has been reduced almost to a minimum. As expected, curve B is asymptotic to curve A, since, in the more concentrated range, hydrolysis of the salt in water alone is very slight.

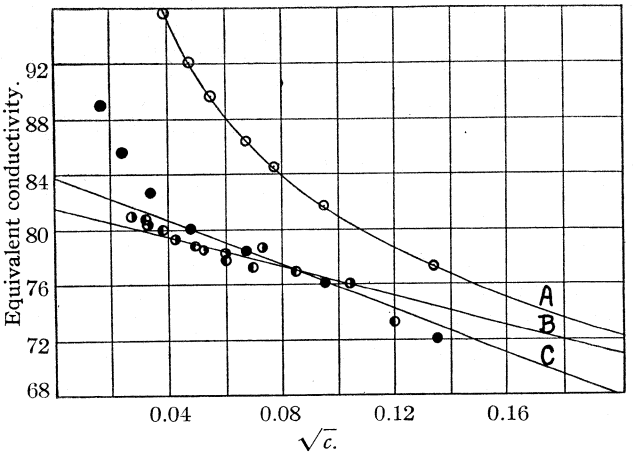


Fig. 2.—The equivalent conductivity of sodium bigermanate at 25°: ⊙, the salt in water alone; ●, 1:1 acid–salt ratio; ◐, 2:1 acid–salt ratio; ◑, 3:1 acid–salt ratio.

Extrapolation of curve B to zero concentration of salt then gives Λ_∞ for sodium bigermanate. This was done on a large scale plot and the value found to be 81.75. This value can then be inserted in the theoretical equation of Onsager[13] for strong electrolytes of the uni-univalent type

$$\Lambda = \Lambda_\infty - \alpha\sqrt{2\mu}$$

where μ is the ionic strength (equal here to the concentration of the salt in moles per liter) and α a constant varying with the electrolyte and equal at 25° to $0.1605\,\Lambda_\infty + 42.28$. Evaluating this constant and introducing it as well as Λ_∞ into the above equation we get

$$\Lambda = 81.75 - 78.3\sqrt{\mu}$$

The experimental slope obtained from the curve was found on the large scale plot to be 79.2, which checks very favorably with the value indicated for α in the above equation. We can, therefore, use the experimental curve and the extrapolated value of Λ_∞ for the salt to calculate the mobility of the bigermanate ion.

The mobility of the sodium ion at 25° was taken as 50.5, as calculated from the value at 18° and the temperature coefficient given in the "I. C. T."[14] Subtracting it from Λ_∞ for the salt, we obtain 31.25 for the value of the bigermanate ion at 25°. This is considerably less than the corresponding

[13] Onsager, *Physik. Z.*, **27**, 388 (1926); *ibid.*, **28**, 277 (1927).

[14] "International Critical Tables," Vol. VI, p. 230.

value for the bicarbonate ion, 46.6, calculated from Kendall's value[15] for Λ_∞ for sodium bicarbonate.

The Dissociation Constant of Germanic Acid.—In order to carry out the required calculations, it is necessary to have values for the equivalent conductivities of the hydrolyzed and unhydrolyzed salt as well as of sodium hydroxide at the same concentration. Inasmuch as the experimental concentrations for the different solutions from which the curves were drawn were not the same, the concentrations chosen for these calculations were those corresponding to the points on curve A for the hydrolyzed salt. The values for Λ' (for the unhydrolyzed salt) at these concentrations were then obtained by interpolation from curve B. Likewise, the values for sodium hydroxide were found by interpolation from a large scale plot of the values given for this substance in the "I. C. T."[16] In Table VI are shown the necessary values used in the calculations together with the values for Λ' calculated from the Onsager equation. Table VII gives the calculated values for the degree of hydrolysis and the hydrolysis constant of the salt and the dissociation constant of germanic acid.

TABLE VI

$\sqrt{c}$	Λ	Λ'_{curve}	$\Lambda'_{\text{calcd.}}$	Λ''
0.1344	77.36	74.05	71.23	230.7
.0950	81.66	76.25	74.31	235.0
.07757	84.49	77.25	75.67	236.4
.06718	86.37	77.85	76.49	237.7
.05485	89.60	78.52	77.45	239.2
.04751	92.03	78.95	78.03	240.1
.03880	95.55	79.48	78.71	241.2

In the fourth column of Table VII are given the values for the ionic product of water at these various concentrations, as interpolated from the values given by Harned[17] and by Harned and Swindells.[18] The value used for zero ionic strength was that determined by Roberts.[19]

TABLE VII

Concn	$100x$	$K_h \times 10^5$	$K_w \times 10^{14}$	$K_1 \times 10^9$
0.01805	2.11	0.823	1.35	1.64
.009025	3.41	1.09	1.19	1.10
.006017	4.55	1.31	1.16	0.89
.004513	5.33	1.35	1.13	.83
.003009	6.90	1.54	1.10	.72
.002257	8.12	1.62	1.08	.67
.001505	9.94	1.65	1.06	.64

[15] Kendall, THIS JOURNAL, **38**, 1480 (1916).

[16] "International Critical Tables," Vol. VI, p. 247.

[17] Harned, THIS JOURNAL, **47**, 930 (1925).

[18] Harned and Swindells, *ibid.*, **48**, 126 (1926).

[19] Roberts, *ibid.*, **52**, 3877 (1930).

Colorimetric Determination of the Dissociation Constant.—Buffer solutions were prepared, as before, containing germanic acid and sodium bigermanate, except that, before the final dilution, the indicator thymol blue was added to the solution. Determinations were carried out with two different samples of indicator of ordinary purity (Hynson, Westcott and Dunning) with no differences in the results. The indicator stock solution was prepared according to the directions given by Clark.[20] Throughout the measurements the concentration of the indicator in the buffers and comparison solutions was kept at 2×10^{-5} mole per liter; while the fully transformed acid and basic forms of the indicator were prepared as described by Kolthoff[21] for the alkaline range of thymol blue. A Gillespie colorimeter was used to determine the acid–base ratio of the indicator in the buffer solutions. From this value and the relationship $[H^+] = K_{Ind.}$ acid/base are obtained the hydrogen-ion concentrations in the various solutions. As the ratios of the salt to the free acid are known for each buffer, simple calculation with the aid of the mass action law gives the dissociation constant of the acid. The observations and calculated results are shown in Table VIII. The values in the third column for the dissociation constants of thymol blue at different ionic strengths were obtained by interpolation from a large scale plot of corrected values for this indicator which were very kindly supplied by Dr. Martin Kilpatrick, Jr.

TABLE VIII

	Concn. of salt	Buffer ratio (acid/salt)	$K \times 10^9$ (T. B.)	Ind. ratio (acid/base)	$[H^+] \times 10^9$	$K_1 \times 10^9$
1	0.01180	1.0	0.980	0.332	0.326	0.326
2	.00944	1.5	.950	.612	.581	.388
3	.00787	2.0	.925	.989	.915	.458
4	.00674	2.5	.900	1.41	1.27	.506
5	.00592	3.0	.880	1.87	1.64	.547
6	.00157	2.0	.700	0.988	0.692	.346

Discussion

The values found for K_1 by the conductimetric method decrease with ionic concentration, as is to be expected on the basis of our present concepts on electrolytic solutions. The reverse seems to be the case for the values obtained colorimetrically. This apparent discrepancy is probably due to the fact that in the solutions studied by the latter method—with the exception of the one numbered 6—the buffer ratio is getting larger from solution to solution, even though the salt concentration is decreasing. In the case of two solutions—for example, 3 and 6—in which the ratio of molecular acid to dissociated salt is the same, the hydrogen-ion concentra-

[20] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 3d ed., 1929, p. 91.

[21] Kolthoff, "The Colorimetric and Potentiometric Determination of *p*H," John Wiley and Sons, New York, 1931, p. 45.

tion as well as the dissociation constant of the acid are found to decrease with decreasing ionic strength. On comparing the values 0.55×10^{-9} obtained colorimetrically with the value 0.89×10^{-9} obtained conductimetrically on a similar 3 : 1 buffer at approximately the same ionic strength, the agreement is found to be fair. The magnitude of the values is, again, of the same order, while the results themselves agree very well with the values close to 1.0×10^{-9} obtained previously by us from conductimetric measurements on solutions of the free acid. The colorimetric method is, of course, limited in its accuracy, but it serves as a very good check on the values obtained by the other and more accurate methods. The fact that the hydrogen-ion concentrations in the buffer solutions studied lie within the range of applicability of this indicator is good indication that the dissociation constants of thymol blue and germanic acid are of the same order of magnitude.

Three methods, independent of each other, were thus used and all gave values in good agreement. The average value of all the determinations—about 1.5×10^{-9}—though somewhat smaller than the value 2.5×10^{-9} reported by Pugh from potentiometric measurements, points rather definitely to the conclusion that values in the neighborhood of 1.0×10^{-7} are considerably in error. We attribute our lower values to a higher degree of purity of the germanic oxide used.

Acknowledgment.—Grateful acknowledgment is made by C. E. Gulezian to the George Leib Harrison Foundation for the fellowship grant which made it possible to carry out this investigation.

Summary

1. Conductimetric titrations of germanic acid with sodium hydroxide have been carried out and indicate the existence in solution of the salt sodium bigermanate.

2. The degree of hydrolysis of this salt at different concentrations has been measured by a conductimetric method, and the dissociation constant of germanic acid calculated from the observations made.

3. The mobility of the bigermanate ion was determined and found to be 31.3 at 25°.

4. Thymol blue was used, in buffer solutions, for the colorimetric determination of the dissociation constant of germanic acid.

5. The average value—approximately 1.5×10^{-9} at 25°—found for the constant by the use of three different methods was compared with the values of other investigators and found to agree with that of Pugh.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

MOLECULAR AND ACTIVATED ADSORPTION OF CARBON MONOXIDE ON MANGANOUS OXIDE SURFACES

BY ARTHUR TANDY WILLIAMSON

RECEIVED APRIL 16, 1932 PUBLISHED AUGUST 5, 1932

During the course of a thorough experimental study of the adsorption of hydrogen on oxides of manganese,[1] an orientation experiment indicated that carbon monoxide behaved in the same general way as hydrogen. The purpose of this communication is to report the results of a comprehensive investigation leading from the earlier observation, and to compare the results obtained with the two gases.

The general theory underlying the experimental work has been given by Taylor,[2] whose paper should be consulted for a comprehensive background. Experimental studies of the adsorption of carbon monoxide on various oxides have been carried out by many,[3] although none of these workers chose the particular surfaces used in this investigation.

Experimental

The preparation of the catalysts and the apparatus was described in the earlier paper.[1] The carbon monoxide used for these investigations was prepared by dropping formic acid into concentrated sulfuric, passing the resulting gas through copper gauze held at 300°, ascarite and phosphorus pentoxide.

Low Temperature Adsorption.—Isothermal adsorption was measured at the temperature of liquid air and again at −78.5°. The results are given in the following tables, which show the amount of carbon monoxide adsorbed in cubic centimeters per gram of catalyst, and which give the resulting equilibrium pressures in millimeters of mercury. All gas volumes were reduced to standard conditions. The general procedure consisted in the preliminary evacuation of the catalyst at 450° and the immersion of the catalyst tube in the desired thermostating medium for several hours to facilitate the attainment of temperature equilibrium. Successive portions of carbon monoxide were then added, readings of the equilibrium pressure being made after each addition. When several points had been obtained desorption was carried out in the same way. The reversibility of an isotherm is shown by the fidelity with which adsorption and desorption points fall on a common curve. In all cases low temperature adsorption was instantaneous.

[1] Taylor and Williamson, THIS JOURNAL, **53**, 2168 (1931).

[2] H. S. Taylor, *ibid.*, **53**, 578 (1931).

[3] See for example Benton, *ibid.*, **45**, 887 and 902 (1923); Taylor and Kistiakowsky, *ibid.*, **49**, 2471 (1927); Markham and Benton, *ibid.*, **53**, 497 (1931); Lazier and Adkins, *J. Phys. Chem.*, **30**, 356 (1926); Schmidt, *Z. physik. Chem.*, **133**, 265 (1928); Garner and Kingman, *Nature*, **126**, 352 (1930).

In addition to the thermostating agents described in a previous paper, use has been made of liquid air, whose temperature could be read continuously by an oxygen vapor pressure thermometer.[4] It was found that an isotherm could be completed in such a bath with a total temperature drift of less than 0.5°.

TABLE I

ISOTHERMS ON 51.3 GRAMS OF $MnO-Cr_2O_3$

Temp., 85.0°K.		85.0°K.		194.5°K.	
P	V ads./m.	P	V ads./m.	P	V ads./m.
0	0.0	32	18.0	0	0.00
1	8.8	58	19.2	6	2.63
2	10.4	87	20.5	20	3.65
3	12.2	118	21.6	62	4.52
4	13.2	91	20.8	132	5.18
5	14.2	68	19.9	227	5.70
8	15.3	47	18.9	332	6.10
17	16.5			177	5.48
				75	4.72
				23	3.82

The isotherm obtained in this manner is difficult to extrapolate to pressures less than 1 mm. If, however, we plot the function P/V against P we obtain a curve which becomes a straight line of the general form $y = mx + b$ below 40 or 50 mm. Disregarding P/V values where P is less than 5 mm. (due to the hypersensitivity of the function in this region), we obtain a straight line which enables us to calculate the equilibrium pressure corresponding to any adsorbed quantity in the low pressure region. In such a manner the values obtained for the pressure given by the adsorption of 3.0 cc. per gram of catalyst were 0.36 mm. and 9.0 mm. at temperatures of 85.0 and 194.5°K., respectively. Substituting these values in the equation

$$\ln P_2/P_1 = \frac{\lambda}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

we obtain $\lambda \cong 980$ cal. This low value is in accord with the idea that this type of adsorption is caused by van der Waals forces.

For the adsorption of 0.1 cc. per gram we obtain pressures of 0.05 mm. and 77 mm. at 83.0 and 194.5°K., respectively. This leads to the following value for the heat of adsorption, $\lambda \cong 2100$ cal.

Due to such complications as capillary condensation of the adsorbate, which is easily condensable in this temperature region, the values given for the heat of adsorption should be accepted only in so far as they give the correct order of magnitude required by non-specific adsorption.

Inspection of the low temperature isotherms of $MnO-Cr_2O_3$ yields the following values for isobaric adsorption at 150 mm. pressure: at 85.0°K.

[4] Stock, *Ber.*, **39**, 2066 (1906).

TABLE II

ISOTHERMS ON 40.3 GRAMS OF MnO

Temp., 83.0°K.		83.0°K.		194.5°K.	
P	V ads./m.	P	V ads./m.	P	V ads./m.
0	0.00	51	4.00	0	0.000
1	1.26	61	4.08	57	.077
2	2.48	70	4.16	79	.102
15	3.52	80	4.25	127	.154
18	3.59	91	4.34	167	.193
29	3.75	389	7.34	222	.251
36	3.83	282	6.31	295	.323
40	3.89	183	5.39	365	.380
45	3.94	15	3.57	424	.425
				493	.473
				296	.325
				141	.166

V ads./m. = 22.5; at 194.5°K. V ads./m. = 5.3. Assuming that the amount adsorbed decreases exponentially with temperature we can show that it will have decreased to less than 2.4 cc. per gram at 306°. The importance of this result will be clear after the high temperature measurements have been presented.

High Temperature Adsorption.—Attempts were made to obtain an isotherm at 218° on MnO–Cr_2O_3, for at this temperature the adsorption should be largely activated. This prediction was realized in part, for large quantities were adsorbed at speeds which were rapid but finite, the amount reaching the following high value.

V ads.	V ads./m.	P
343.5	6.70	172

However, it was impossible to obtain true equilibrium values, for after the rate had died down to a certain point it drifted steadily for weeks without any marked diminution in magnitude. The reason for this drift with carbon monoxide became apparent when a similar experiment was made at 306°. Once more the rate dropped from its initially high value to one which showed no signs of approaching zero. After five weeks' contact the adsorption reached the following value.

V_T[5]	V_{DS}	V ads.	V ads./m.	P
276.0	4.3	271.7	5.29	90

The temperature was then raised to 450° and the gas was removed from the catalyst chamber by the Sprengel pump for measurement and analysis. The results are tabulated below.

[5] These abbreviations have the following meanings: V_T = total volume of gas in the catalyst tube; V_{DS} = volume required to fill the "dead space"; V ads. = the difference of the above two, *i. e.*, the amount adsorbed. V ads./m. = adsorption per gram of catalyst.

TABLE III

ADSORPTION OF CO ON $MnO-Cr_2O_3$ AT 306°

Carbon monoxide introduced, 276.0 cc. Gas recovered by Sprengel pump, 273.4 cc.

Sample no.	Analysis of recovered gas CO	CO_2	%, CO_2
1	33.2	8.4	20.2
2	18.7	6.3	25.2
3	38.2	14.3	27.2
4	36.4	16.5	31.2
5	41.1	18.0	30.5
6	23.1	19.2	45.4
	190.7	82.7	30.3

There are two ways in which the carbon dioxide may be formed; by the reaction $2CO \longrightarrow C + CO_2$ or by actual reduction of the catalytic surface. Since the total volume of the recovered gases was practically equal to the amount of carbon monoxide originally introduced, it is evident that the former mechanism is excluded. We are, therefore, forced to the conclusion that reduction of the catalyst has taken place. It is to be observed that the proportion of carbon dioxide increases as the desorption advances.

The reduced catalyst was next reconditioned by oxidizing it in air at 300° and reducing with hydrogen at the same temperature. It was pumped off thoroughly at 450°. The influence of the time factor on reduction of the stable oxides was then studied by adsorbing a fairly large quantity of carbon monoxide at 306° and cleaning the surface with the Sprengel pump as rapidly as possible.

TABLE IV

ADSORPTION OF CO ON $MnO-Cr_2O_3$ AT 306°

Time of adsorption = two hours

V_T	V_{DS}	V ads.	V ads./m.	P
172.5	6.4	166.1	3.22	134

	Analysis of recovered gas CO	CO_2	%, CO_2
1. Desorption at 306°, 12 hours	115.9	0.9	0.8
2. Desorption at 450°, 8 hours	41.2	16.2	28.2
	157.1	17.1	9.8
Carbon monoxide introduced		172.5	
Gas recovered		174.2	

The marked rise in the yield of carbon dioxide with the rise in temperature shows that this is the main factor in the reduction of the catalyst, and that an activated adsorbate does not necessarily yield a reduced surface unless the temperature is high enough. Since the 57.3-cc. sample collected at the higher temperature did not yield as high a proportion of carbon dioxide as did the similar final portion collected after the five-week run, we

may conclude that reduction of the catalyst will take place at 306°, but only at a rate which is very small compared with the velocity of activated adsorption. Both rates are increased tremendously by raising the temperature.

On MnO an attempt was made to measure an isotherm at 444°, but the same difficulties intervened. After three weeks of contact the following values were obtained.

TABLE V

CO ON MnO AT 444°

V_T	V_{DS}	V ads.	V ads./m.	P
41.3	17.2	24.1	0.60	447

Analysis of desorbed gas

CO	CO_2	% CO_2
7.9	29.1	78.6

Carbon monoxide introduced	41.3
Gas recovered	37.0

The reduction is startlingly evident. Furthermore, the apparent decrease of 4.3 cc. in the total volume is significant, for the quantities of gas admitted normally agree with the amounts collected by the Sprengel pump within ±1%. In this case there is a drop of some 10%, so the reaction $2CO \longrightarrow C + CO_2$ may have been proceeding simultaneously with the ordinary surface reduction by the carbon monoxide.

Rates of Adsorption.—In the investigation of the adsorption of hydrogen on these catalysts it was easy to separate the two types because adsorption of the molecular sort was relatively very small, and was negligible in the temperature range where the activated adsorption was occurring with a measurable velocity. With carbon monoxide the van der Waals forces are larger, so the molecular adsorption overlaps the activated form at all temperatures suitable for rate measurement. For this reason it was impossible to measure the activation energy required to adsorb carbon monoxide in the activated form.

General

Although the order given in this paper would indicate that the low temperature measurements were the first to be made, this was so only with the unpromoted MnO. On the mixed oxide surface all the high temperature measurements were completed before the isotherms at −78.5 and −190° were investigated. This is very important in the light of a suggestion[6] recently made which attempts to explain activated adsorption as a slow chemical reaction which removes impurities from the surface, thereby leaving a larger area available for adsorption purposes.

The experimental facts actually obtained are not in accordance with

[6] Allmand and Chaplin, *Trans. Faraday Soc.*, **28**, 223 (1932).

such a theory, for the early attempts to obtain an isotherm at 218° led to an adsorption value of 6.70 cc. per gram of $MnO-Cr_2O_3$. Later, when the isotherm at −78.5° was measured it was found that the quantity adsorbed per gram at the same pressure (172 mm.) was about 5.4 cc., a marked decrease instead of a very large increase. Additional evidence against the theory has been given in Table IV, where it was shown that of 166.1 cc. of gas adsorbed in the activated form not more than 17.1 cc. could be attributed to a combination with the surface to give carbon dioxide, and that the maximum possible "molecular" adsorption would be 2.4 cc. per gram, or 127 cc. in all.

In the experiments with hydrogen reported in the earlier paper,[1] high temperature runs on both catalysts were completed before the molecular adsorption was measured, and in that case the activated adsorbate was far greater in magnitude than any of the low temperature molecular values.

In conclusion the writer wishes to thank Professor Hugh S. Taylor for his interest in the prosecution of this work, and for his part in the planning of the experimental procedure leading to the results given above.

Summary

1. The adsorption of carbon monoxide on MnO and $MnO-Cr_2O_3$ has been measured between −190 and +444°.

2. The adsorption takes place in two forms: a molecular form at low temperatures with zero energy of activation and a heat of adsorption of 1000–2000 calories and an activated form which becomes evident above 0°. The former is easily pumped off, the latter is very difficult to recover.

3. Unlike hydrogen, the activated carbon monoxide adsorbate causes partial reduction of the catalyst. It has been found, however, that this reduction is slow compared with the velocity of activated adsorption, and as much as 90% of the activated adsorbate has been recovered unchanged.

4. Overlapping of the two types prevented measurement of the velocity of adsorption, so it is impossible to give any values for the activation energy of the high temperature process.

5. These oxides do not catalyze the reaction $2CO \longrightarrow C + CO_2$ to any measurable extent below 300°, although evidence points to its possible occurrence on MnO at 444°.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

THE PHOTOLYSIS OF THE ALIPHATIC ALDEHYDES. I. PROPIONALDEHYDE

BY PHILIP A. LEIGHTON AND FRANCIS E. BLACET

RECEIVED APRIL 20, 1932 PUBLISHED AUGUST 5, 1932

The application of atomic mechanics to the processes following upon the absorption of light has met with some success in the case of diatomic molecules, in elucidating the nature of photochemical activation and reaction mechanism. In applying to polyatomic molecules some of the principles of photochemical activation and reaction mechanism which have arisen from the study of diatomic molecules, one of the most promising fields is offered by the aliphatic aldehydes, which, starting with formaldehyde, are only a step more complicated than a diatomic molecule of the oxygen type.

The absorption spectra of the aldehydes in the region 2500–3500 Å. have been studied by Victor Henri and his collaborators[1] who have shown that in every case the three typical regions of absorption; bands with fine structure, diffuse bands or predissociation, and continuous absorption, are found as one goes from long to short wave lengths. The different regions merge into each other, and the first two are overlaid with a faint continuous absorption.

The work of a number of observers[2] has shown that the simpler aldehydes are all decomposed by the absorption of light in this region. The reaction proceeds principally in two ways: first, a direct decomposition into carbon monoxide and the corresponding hydrocarbon, RHCO = RH + CO; and second, a polymerization into complex solid products. Attempts to detect the presence of other gases, such as hydrogen, carbon dioxide, oxygen or water vapor in the products of decomposition have shown that they are either totally absent or, if present, are found in only very small amounts.

An investigation by J. H. C. Smith and Victor Henri[3] into the kinetics of the reactions has shown in the case of acetaldehyde that the governing rate of the decomposition is unimolecular, while the governing rate of the polymerization is bimolecular.

It is a matter of interest, in view of recent interpretations of the phenome-

[1] Henri, *Trans. Faraday Soc.*, **25**, 765 (1929); Henri and Schou, *Z. Physik*, **49**, 774 (1928); de Hemptinne, *J. phys. radium*, [VI] **9**, 357 (1928).

[2] Berthelot and Gaudechon, *Compt. rend.*, **151**, 478 (1910); **156**, 68 (1913); Bredig and Goldberger, *Z. physik. Chem.*, **110**, 532 (1924); Bowen and Watts, *J. Chem. Soc.*, **129**, 1607 (1926); Henri and Wurmser, *Compt. rend.*, **156**, 230 (1913); *J. phys. radium*, [VI] **8**, 289 (1927); Volmer, *Compt. rend.*, **178**, 697 (1924); Norrish and Griffiths, *J. Chem. Soc.*, 2829 (1928); Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

[3] Smith, *Carnegie Inst. Reports*, **27**, 178 (1928).

non of predissociation,[4] to correlate, as far as is possible, the spectroscopic data with the photochemical reactions produced. In particular the influence of wave length changes on the two reactions should be investigated. Several approximate measurements of the influence of wave length have been made. De Hemptinne,[1] working on benzaldehyde, found that the decomposition into benzene and carbon monoxide did not occur at wave lengths longer than the limit of the diffuse spectrum. Kirkbride and Norrish[2] have recently made similar tests on formaldehyde, and have reached the same conclusion regarding its decomposition. Smith[3] studied the effect of wave length on both the decomposition and polymerization of acetaldehyde vapor. He found that polymerization was effected by light throughout the absorption region, but that the decomposition proceeded rapidly only in the region of continuous absorption.

Since these measurements were all made with the use of light filters, which can give only an approximate separation of the different regions, and since none involved an accurate measurement of quantum yields, the authors have undertaken a series of quantitative measurements in monochromatic light on a number of the aldehydes. The present paper describes the experimental method, and the results on propionaldehyde. In a subsequent paper, a study on acetaldehyde will be reported, and a correlation between spectroscopic and photochemical data proposed.

2. Apparatus and Method

(a) Monochromator.—The ultraviolet radiation was obtained from a high pressure quartz mercury arc of the type perfected by Forbes, Harrison, P. A. Leighton and W. G. Leighton.[5] These arcs give very constant and intense illumination. The one employed in this research has been used frequently for runs of over twelve hours duration without appreciable fluctuation of intensity although no adjustments of any kind were made during this time.

Monochromatic light was obtained by means of a fused quartz prism and lenses, as shown diagrammatically in Fig. 1. Section A outlines the box, drawn to scale, which housed the arc and monochromator. Light from the arc entered the collimating slit S and, after passing through the prism and lenses, had its various components focused along the dotted line F. The entire box A was movable so that any desired line of the mercury spectrum could be brought to a focus upon the second slit S′. This was facilitated by pivoting the box beneath the lens L′. The pivot pin fitted in a channel which was in direct line with S′. This made it certain that the light entering section B was always traveling in the same direction.

---

[4] Henri, *Nature*, Dec. 20, 1924; *Trans. Faraday Soc.*, **25**, 766 (1929); Born and Franck, *Z. Physik*, **31**, 411 (1925); Franck and Sponer, *Göttinger Nachr.*, 241 (1928); Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1927); Herzberg, *Trans. Faraday Soc.*, **25**, 778 (1929); **27**, 378 (1931); *Z. Physik*, **61**, 604 (1930).

[5] Harrison and Forbes, *J. Opt. Soc. Am.*, **10**, [1] 1 (1925); Forbes and Harrison, *ibid.*, **11**, [2], 99 (1925); Forbes and Leighton, *ibid.*, **12**, [1], 53 (1925); Forbes and Harrison, THIS JOURNAL, **47**, 2449 (1925); W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

The equilateral prism P was of fused silica 6.5 cm. high and 9.5 cm. on a side. The lenses L and L′ were of the same material and 7.5 cm. in diameter. Their focal lengths were approximately 21 cm. for yellow light. L was placed 20 cm. from the slit S. The monochromator had a curved collimator slit, 1.5 mm. by 30 mm. in size, which gave a rectilinear image.

Section B, Fig. 1, was a thermostatically controlled box containing, primarily, the absorption tube R and the thermopile T. The slit S′ was of adjustable knife edges, 3 cm. high. It was maintained at 1 mm. in width in this work. A black screen was placed in front of R. The opening in this was made sufficiently small so that no light could enter directly into the walls of the tube.

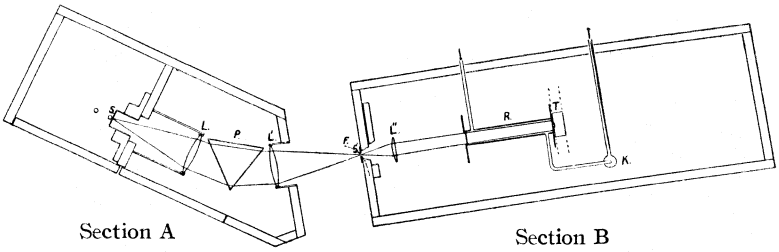


Fig. 1.—Diagram showing the path of monochromatic light.

(b) The Gas Train.—It was found that the common stopcock lubricants cause polymerization of propionaldehyde vapor. Mercury, on the other hand, in the absence of oxygen has no effect on the aldehydes. Accordingly, a gas train was constructed in which the aldehyde vapor at no time came in contact with any material except mercury, Pyrex glass and fused silica. Figure 2 is a diagrammatic sketch of this arrangement. A was a storage bulb for the substance being investigated. B and C, with the vertical tubes above, were mercury gas traps. R represents the absorption chamber. K was a liquid air trap. That part of the diagram designated by M, N, O, O′, Q, U, Y and W was a gage for measuring small changes in pressure during an exposure.

The operation of the traps B and C is obvious, except that in order to open them it was necessary to have the mercury standing at the same level in the two arms of the U-tube, as vacuum was being applied to the flask. This was accomplished by using liquid air to reduce the vapor pressure either in A or R as might be required. The right-hand vertical tube of trap C led to a Toepler pump and the gas analysis apparatus.

The absorption chamber R was 20 cm. long and 3 cm. in diameter. It was made entirely of fused quartz and was connected to the rest of the apparatus by means of Pyrex-to-silica graded seals. The ends were of plain quartz fused in place. An attempt was made to use a glass tube with quartz windows sealed on with chicle cement. This plan was abandoned, however, when it was found that propionaldehyde vapor condenses rapidly to a liquid upon coming in contact with this cement.

(c) The Pressure Gage.—In order to measure the small changes in pressure during photolysis, the differential pressure gage diagrammed in Fig. 2 was employed. This was an adaptation of the type described by Pearson.[6] M was an evacuated bulb, having two sealed-in tungsten electrical contacts. The tip of the upper one of these was accurately centered in the bulb. A dry cell and relay completed the circuit. A condenser was used across the relay terminals to prevent sparking.

N was a tube of uniform bore and 13.1 mm. diameter. O was a uniform capillary tube having a volume of 0.867 cu. mm. per linear mm. This was mounted upon a milli-

[6] Pearson, *Z. physik. Chem.*, **A156**, 86 (1931).

meter scale. O′ was a 300-cc. bulb, which acted as an air cushion and permitted a sensitive adjustment of the mercury height in the capillary O.

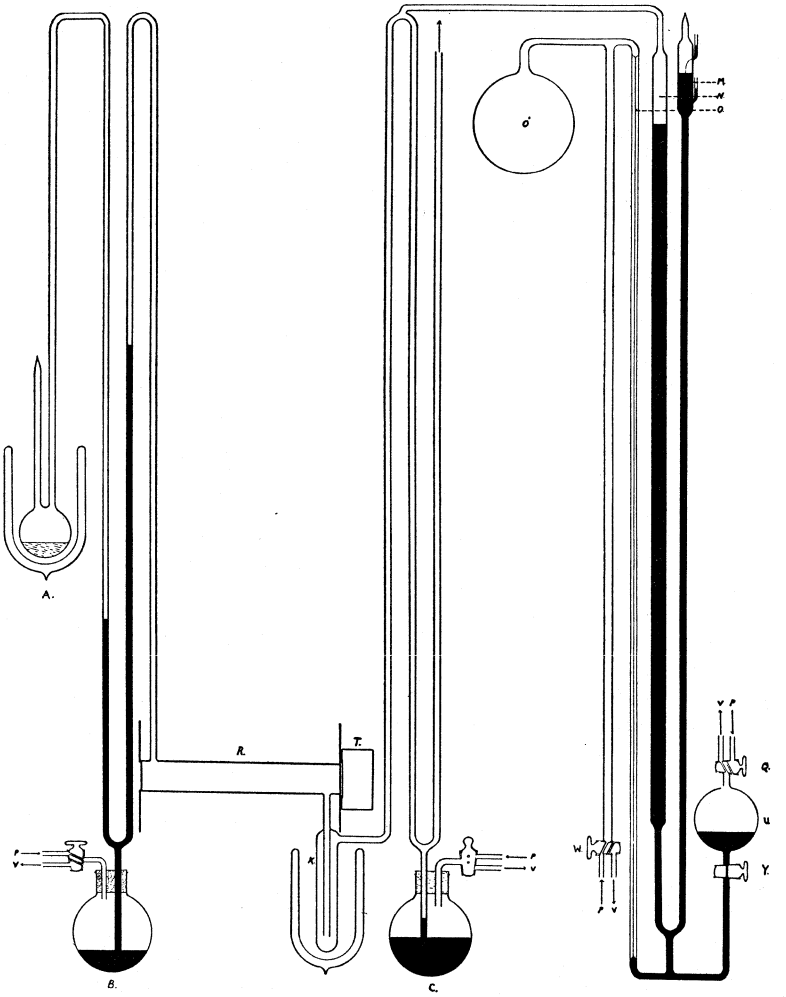


Fig. 2.—Diagram of the essential features of the gas train and the pressure gage.

At the beginning of a run, mercury was brought to a convenient height in the capillary by operating the two-way stopcock W, which was open to the atmosphere and also connected to the vacuum line. Mercury was then brought just to the point of electrical contact in M by the proper manipulation of stopcocks Q and Y. Following this, Y was closed, leaving a definite amount of mercury in the system, MNO. In these adjustments the mercury in N automatically came to a certain level, depending upon the pressure in the absorption tube R.

With the traps B and C closed (but their stopcocks open to the atmosphere), the volume of gas in RKN was fixed. (Volume change in the small columns of the traps

due to fluctuating atmospheric pressure was negligible with respect to the total volume of the gas.) Any change in pressure in the system due to a reaction in R caused a variation of the mercury level in N. Let it be supposed that there was a slight increase in pressure in the system. Since the space above the mercury in M was evacuated, the system MN acted in the same manner as a barometer and there was a definite completion of the relay circuit. Now by applying vacuum at W, the mercury level in O was raised, drawing mercury from M until the level there was again just at the point of "make and break." Since the level in M was back then to the original point, the extra mercury drawn into O came from N. From the change in height of the column in the capillary and from the volume ratio per unit length of the tubes N and O, the pressure change in the system RKN was calculated. One mm. change of the mercury height in O was equivalent to 0.00642 mm. pressure change in the reaction system.

In practice, pressure gage readings were taken at frequent intervals during an exposure. These values were plotted against time and from the curve obtained in this way the total pressure change in the system during an exposure was obtained with a certainty of ± 0.01 mm.

The temperature of the system RKN was controlled to within 0.1 of a degree. The volume, which varied with the pressure, could always be calculated. The total pressure in the system was obtained from a metric scale placed between the two arms of the Y tube of trap C. This was permissible since the tube leading to the Toepler pump was always highly evacuated during an exposure.

(d) **Energy Measurements.**—The thermopile used in this work was made by one of us. It contained twenty bismuth to silver "hot" junctions with blackened tin foil radiators. It was of the line type, having an exposed sensitive surface 3.0 mm. wide and 30.50 mm. high. A thin crystal quartz window protected the junctions from air currents and dust. As indicated in Fig. 1, the thermopile could be moved horizontally across the rear window of the absorption tube R. This movement was effected by means of a machined screw with 1 mm. pitch. A high sensitivity galvanometer (Leeds-Northrup, type 2285-X) was used with the thermopile. This was mounted in a heavy Julius suspension and at the center of curvature of a millimeter scale five meters away.

This thermopile–galvanometer system was calibrated in the manner previously described.[7] In addition to the sensitivity of the thermopile as a whole, the integrating ability of aliquot portions of its length was tested in the manner described by W. G. Leighton and G. S. Forbes.[5] The mean deviation in sensitivity along the sensitive surface was found to be $\pm 4\%$. Corrections were found for only the first and last thermopile readings, and since these readings were always of small magnitude (being taken on the edge of the beam), the corrections could be neglected without appreciable error. The sensitive surface of the thermopile was sufficiently long to extend slightly above and below the widest portion of the light beam coming through the absorption tube. Since the thermopile slit was 3 mm. in width, the total emergent energy, ΣB, was integrated by moving the thermopile across the back of the absorption tube in steps of 3 mm. each.

(e) **Calibration of the Absorption Tube.**—In order to obtain the amount of energy absorbed by a gas in the reaction chamber, it was not sufficient to calculate the difference between the total radiation passing through the tube when it was full and when it was empty. A certain fraction, x, of the light entering the tube was lost through the walls because of imperfections in the optical train. This loss was due principally to the fact that a line source, instead of a point source, of radiation was used.

[7] Leighton and Forbes, THIS JOURNAL, **51**, 3549 (1929).

It can be shown that this fraction x is given for each wave length by the expression

$$x = 1 - \frac{J_t}{b^2 J_0} \quad (1)$$

in which J_0 is the energy incident on the front window of the cell, J_t is the energy emerging from the rear window, and b is the fraction of incident monochromatic light transmitted by a single quartz window in air. The values for b may be obtained from indices of refraction of the various wave lengths and the application of Fresnel's law. Experimentally, for each of the strong lines of the mercury arc, J_t was obtained in the manner which has been described and J_0 was ascertained by removing the quartz reaction tube and placing the thermopile and its track up so that its window was in the same plane as was previously occupied by the front window of the tube. By integrating the beam which came through the black screen, which was now immediately in front of the thermopile, the correct value of J_0 was secured. Once determined for an experimental set-up, x becomes a constant in the calculation of quantum efficiencies (see equation 2).

(f) **Method of Analysis.**—The method of microanalysis employed has been described in detail elsewhere.[8] In spite of the fact that liquid air was used to condense the surplus aldehyde vapor, a small amount of this substance was always present in the gaseous decomposition products. In order to remove it, a solid potassium hydroxide bead was introduced into the gas by the method previously described. This reagent caused rapid polymerization of the aldehyde to a resin-like substance which adhered to the bead and was removed with it from the gas sample.

The amount of carbon monoxide produced in decomposition was taken as an index of the number of molecules of aldehyde which decomposed. Solid silver oxide was used to absorb the carbon monoxide. A complete description of the use of this absorbent will be given in another article. The volumes of gas used for analysis varied between 50 and 100 cu. mm. Check determinations were made in all cases, and for eighteen consecutive samples from different exposures, the average deviation from the mean per cent. of carbon monoxide for each sample was 0.26% absolute.

In the study of the mechanism of decomposition, it is important to know whether or not hydrogen is produced and, if so, to what extent. The principal hydrocarbon found in the decomposition of propionaldehyde is ethane. If hydrogen is formed there should be an equivalent amount of butane formed also. Since these hydrocarbons are solids at liquid air temperatures, an attempt was made to separate the carbon monoxide and hydrogen from the ethane and butane by thoroughly cooling the trap K (Fig. 2) and pumping off the carbon monoxide and hydrogen in a minimum number of operations of the Toepler pump. Although some of the hydro-

[8] Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

carbons came over in the pumping, there was a sufficient enrichment of the hydrogen content so that an analysis for it could readily be made. The carbon monoxide was first removed and then the residue was analyzed by explosion for hydrogen and ethane, the assumption being made that the butane remained in the liquid air trap.

It is well known that silver oxide reacts with both hydrogen and carbon monoxide and, theoretically, its use as an absorbent introduced an error in the percentages of these gases found to be present. However, dry silver oxide reacts much more slowly with hydrogen than it does with carbon monoxide. By means of a series of experiments with known mixtures of these gases, it was found that in the time necessary to remove all the carbon monoxide in a sample containing 90% CO and 10% H_2, not more than 2.5% of the total amount of hydrogen could be absorbed. Since 10% H_2 is above the maximum amount experimentally found in photolysis (see Table II), it may be reasoned that 0.25% absolute represents the maximum error due to this cause.

(g) **Calculations.**—L_0, the amount of light which entered the absorption tube per second, is given by the equation

$$L_0 = \Sigma B_I \times \frac{1}{b} \times \frac{1}{1 - x} \tag{2}$$

and L_t, the energy reaching the rear window per second, by

$$L_t = \Sigma B_L \times \frac{1}{b} \tag{3}$$

ΣB_I is the total ergs per sec. emerging from the rear window of the empty tube and ΣB_L is this summation when the tube contains the absorbing gas. In the calculation of each of these quantities a factor was introduced which corrected for the difference in transmission of the quartz thermopile window for the wave length used as compared to its transmission for the mean wave length of the light from the carbon filament standard lamps.

It can be shown that Q and Q', the fraction of L_0 absorbed by the original vapor at the beginning and at the end of an exposure, are given respectively by the expressions[9,7]

$$Q = (1 - L)(1 + rL) \frac{\log L - \log I}{\log L} \tag{4}$$

and

$$Q' = y(1 - L)(1 + rL') \frac{\log L - \log I}{\log L'} \tag{5}$$

in which $L = L_t/L_0$, $I = 1-x$, L' is the fraction of L_0 reaching the rear window at the end of an exposure, r is the fraction of light striking the rear window which is reflected back into the reaction system, and y is the fraction of the original gas remaining in the reaction chamber. In the evaluation of y, the assumption was made that in polymerization a trimer

[9] Luther and Weigert, *Z. physik. Chem.*, **53**, 408 (1905).

was formed which remained in the gaseous state. The error introduced because of this assumption cannot be large, for in all cases y was only slightly less than 1.0.

In this research it was found that L and L' were equal, within about 1%, for all runs. Since this is within the limits of experimental errors

$$Q' = yQ \tag{6}$$

and from previous study[7] the average fraction of the light entering the tube absorbed during a run

$$Q_m = \sqrt{QQ'} = Q\sqrt{y} \tag{7}$$

The total quanta absorbed is given by

$$\text{Quanta} = \frac{L_0 S Q_m}{h\nu}$$

in which S represents the time in seconds and $h\nu$, of course, the energy per quantum. Φ_d, the quantum efficiency of decomposition, was taken as the ratio of the molecules decomposed to the total quanta absorbed (*i. e.*, Φ_d = molecules decomposed/quanta absorbed).

It was impossible to determine the polymerization products of photolysis (see experimental results); therefore, in order to obtain some basis for the comparison of the amounts of polymerization at different wave lengths or pressures, a quantum yield of apparent polymerization was adopted. This value was obtained by calculating the decrease in molecular concentration during an exposure which was due to polymerization and dividing this by the number of quanta absorbed. The total molecular change in the system was secured from the pressure gage readings. Each decomposing molecule caused an increase of one molecule in the system. Therefore, molecules apparently polymerized = molecules decomposed − (± total molecular change). From this was calculated the quantum efficiency of *apparent polymerization*.

$$\Phi_p = \frac{\text{molecules apparently polymerized}}{\text{total quanta absorbed}}$$

3. Experimental Results

In the study of propionaldehyde, five lines of the mercury arc, ranging from 2537 to 3130 Å., were used for monochromatic radiation (Table I). As shown in Fig. 3, these lines cover fairly uniformly the region of maximum absorption which is attributed to the carbonyl group. In this graph, the average value of Q_m at 200 mm. pressure is plotted against the wave length of light employed.

The variations of both the decomposition and apparent polymerization quantum yields (Φ_d and Φ_p, respectively) with wave length, are given in Fig. 4. The points shown in each case are the average of two or more values obtained with an approximately constant pressure of 200 mm. in the reaction system.

TABLE I

EXPERIMENTAL DATA FOR QUANTUM YIELDS

λ, Å.	Pressure, mm.	L_0 erg./sec.	Quanta absorbed × 10^{18}	Molecules decomposed × 10^{18}	Mol. appar. polymerized × 10^{18}	Φ_d	Φ_p
2537	203	1860	3.68	3.33	..	0.905	..
	204	1420	3.39	3.76	2.57	1.11	0.758
	196	1469	3.21	3.11	2.43	0.970	.757
	196	4175	8.15	8.86	6.01	1.09	.737
2654	202	2880	4.89	3.84	3.84	0.785	0.785
	203	2600	4.31	3.28	..	.761	..
	204	2251	5.20	3.86	3.91	.742	.751
	89	8235	13.20	10.40	3.49	.787	.264
	33	8560	6.59	4.97	0.58	.754	.086
	14	8565	4.65	3.30	0.04	.723	.066
2804	199	3970	13.15	9.31	8.50	0.708	0.646
	196	4350	11.81	8.22	7.42	.695	.628
3020	196	7800	14.50	7.51	..	0.518	..
	207	7000	14.33	8.09	..	.564	..
	203	5950	10.30	6.11	6.11	.594	0.594
	211	5870	10.50	5.60	5.60	.533	.533
3130	195	13600	29.80	15.71	22.78	0.527	0.764
	192	8485	12.87	6.40	9.80	.497	.763
	74	27500	27.56	14.90	7.32	.540	.266
	36	11620	13.40	7.57	1.80	.565	.134
	13	12340	7.53	4.16	0.26	.552	.034

At two different wave lengths (2654 and 3130 Å.) the variations of quantum yields with pressure were determined. In Fig. 5, it may be observed that Φ_d at both wave lengths has a nearly constant value over the pressure range of 13 to 200 mm. Polymerization, on the other hand, increases steadily over this range.

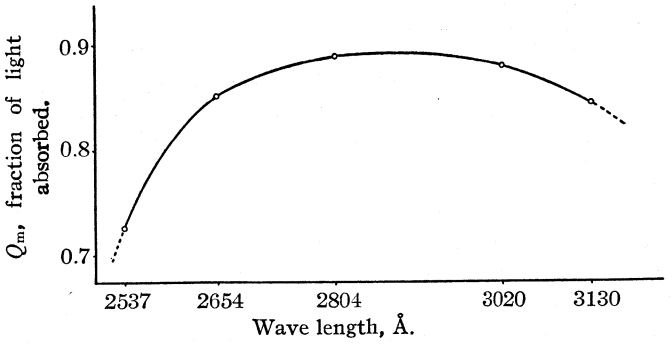


Fig. 3.—Fraction of light absorbed, Q_m *vs.* wave length, at 200 mm. pressure.

A constant temperature of 30° was used for all determinations of quantum efficiencies.

TABLE II

HYDROGEN FROM PROPIONALDEHYDE DECOMPOSITION

λ, Å.	Pressure, mm.	Analysis	Vol. CO, cu. mm.	Vol. H_2, cu. mm.	H_2, %	Average % H_2	% C_2H_5CHO molecules yielding H
2537	196	1	328.2	14.1	4.6	4.4	8.8
		2	328.2	13.0	4.2		
2654	89	1	384.8	28.0	7.3	8.8	17.6
		2	384.8	39.6	10.3		
3130	14	1	569.2	23.6	4.1	4.2	8.4
		2	569.2	24.5	4.3		

The presence of hydrogen in the decomposition products was confirmed for three different wave lengths as shown in Table II. In calculating the percentage of decomposing propionaldehyde molecules which produced hydrogen, it was assumed that only one hydrogen atom was expelled from each molecule. As shown by Table II, at a pressure of 14 mm. where the polymerization reaction has practically ceased, the amount of hydrogen produced is still comparable with that at higher pressures. Accordingly, it is assumed that the hydrogen production accompanies the decomposition reaction only.

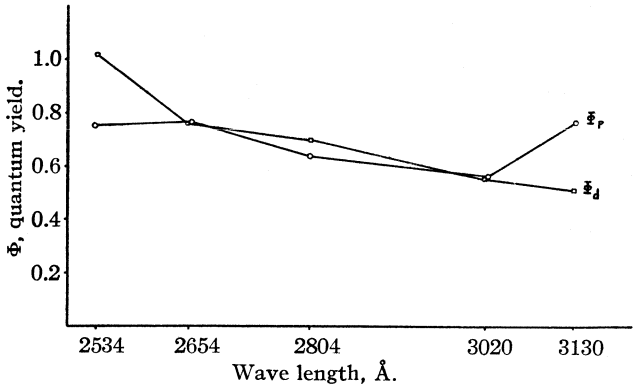


Fig. 4.—Variations of decomposition (Φ_d) and apparent polymerization (Φ_p) quantum yields with wave length, at 200 mm. pressure.

The fluorescence of propionaldehyde vapor could only be studied qualitatively because of the varying intensity of the mercury lines. However, marked fluorescence was present when the vapor was exposed to all wave lengths down to and including the λ2654 Å. line. It apparently decreased in intensity with decreasing wave length, and when the aldehyde was exposed to the λ2537 Å. line it was absent.

The only evidence obtained in regard to the nature of the polymerization products was (1) a very slight cloudiness which appeared on the walls of the quartz absorption tube; and (2) the percentage of light absorption did not

decrease appreciably during an exposure. These observations indicate either that a mixture of different polymers is formed or that if a single substance is the product, it has a high vapor pressure at 30°.

4. Discussion

Upon examination of the curves in Figs. 4 and 5, it is observed that the quantum yield of decomposition, Φ_d, increases with decreasing wave length, from a value of 0.51 at λ3130 to 1.02 at λ2537, with a sharp rise between λ2654 and 2537. The apparent quantum yield of polymerization, Φ_p, shows variable behavior with changing wave length. Between λ3130 and 3020 it drops rapidly, then rises at about the same rate as the decomposition to λ2654, while between λ2654 and 2537 it does not change.

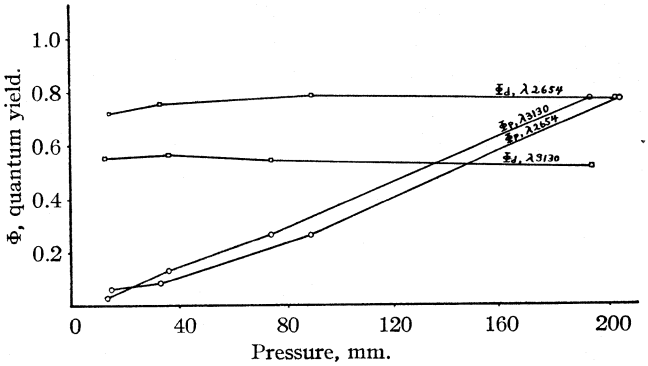


Fig. 5.—The effect of the variation of pressure upon decomposition (Φ_d) and polymerization (Φ_p) quantum yields.

The variations in quantum efficiencies with pressure (Fig. 5) are of especial interest. At two widely different wave lengths, decomposition appears to be a unimolecular process, the quantum yield being independent not only of the pressure but also of the amount of polymerization. The polymerization quantum yield, on the other hand, is zero at zero pressure and increases in direct proportion to the pressure. This suggests that the governing rate of the polymerization is bimolecular, in agreement with the findings of J. H. C. Smith for acetaldehyde.[3] It should be emphasized that the decomposition quantum yields represent the true values, since they maintain their constancy at low pressures, where the rate of polymerization has approached zero.

All of the evidence earlier quoted, together with that found in this Laboratory, indicates that in the decomposition of the aldehydes the principal reactions may be represented by

$$\mathrm{RHCO} + \text{light} \begin{cases} \nearrow \mathrm{RH} + \mathrm{CO}\ (80\%\ \text{or more}) \\ \searrow \tfrac{1}{2}\mathrm{R_2} + \tfrac{1}{2}\mathrm{H_2} + \mathrm{CO}\ (20\%\ \text{or less}) \end{cases}$$

In their study of the absorption spectra of the aldehydes, Henri and Schou[10] have found that with increase in molecular weight it becomes more and more difficult to analyze the spectral structure. For propionaldehyde they were able to detect discontinuous absorption only between 3400 and 3250 Å. The bands were faint, very diffuse, close together and became more and more indistinguishable toward shorter wave lengths, merging apparently into a continuum in the neighborhood of 3250 Å.

Herzberg[4] has reviewed the work of Henri and Schou on formaldehyde and on the basis of theoretical reasoning has suggested that the primary product of predissociation is represented thus

$$H_2CO + h\nu = H + CHO$$

The application of this to the higher aldehydes gives two possibilities

$$RHCO + h\nu = RCO + H$$
$$\text{or } RHCO + h\nu = HCO + R$$

Although studies of the energies of dissociation of the C—H and C—C bonds result in values of 90,000 to 110,000 calories for the former and 70,000 to 90,000 calories for the latter,[11] all measurements agree that the C—C bond energy is about 15,000 to 20,000 calories less than that of the C—H bond. Hence it may be assumed that in the higher aldehydes the C—C bond is broken and the decomposition occurs principally according to the second equation above.

In this regard, it is interesting to observe that, if the dissociation of formaldehyde by light involves the breaking of a C—H bond, while the dissociation of acetaldehyde involves a C—C bond, by the theory of Herzberg the long wave length limit of predissociation in each case should set an upper limit for the energy of dissociation of these bonds. The predissociation limits and corresponding energies in each case are:

	Bond	λ	Upper limit of diss. energy	Thermal bond energy[12]
Formaldehyde	C—H	2750 Å.	103,000 cals.	98,500
Acetaldehyde	C—C	3200 Å.	89,000 cals.	87,600

With regard to the secondary reaction, the simplest course of the decomposition would be represented by

$$RHCO + h\nu = HCO + R \quad (1)$$
$$HCO + R = RH + CO \quad (2)$$
$$HCO + HCO = H_2 + 2CO \quad (3)$$
$$R + R + X = R_2 + X \quad (4)$$
$$HCO + R + X = RHCO + X \quad (5)$$

[10] Schou, Doctorate Thesis, Les Presses Universitaires de France, Paris (1928); Henri and Schou, *Z. Physik*, **49**, 774 (1928).

[11] Andrews, *Phys. Rev.*, **36**, 544 (1930); F. O. Rice, *Chem. Rev.*, **10**, 135 (1932); Hogness, paper presented at the Indianapolis meeting of the American Chemical Society, April, 1931; Mecke, *Z. physik. Chem.*, **B7**, 108 (1930).

[12] L. Pauling, personal communication.

Experimental findings on the relative amounts of RH and of H_2 produced would indicate that the probability of reaction 2 occurring is of the order of five to ten times that of reactions 3 and 4. Since the rate of all these reactions is dependent only on the amount of dissociation, the quantum yield of decomposition should be independent of the pressure, as it is.[13] A recombination, as by reaction 5, is indicated by the low decomposition quantum yields at wave lengths between 3020 and 2654 Å.

It is difficult to reconcile the existence of polymerization at all wave lengths, as well as the observation of fluorescence down to λ2654 Å., with a pure dissociation spectrum, as is indicated by the continuous absorption below 3250 Å. It is possible that banded absorption, with the production of activated molecules, extends to much shorter wave lengths than 3250 Å., and is not observable because of the fineness of the bands and the overlaid continuum. The reactions produced by absorption in this banded, overlaid continuum region would be, in addition to the decomposition reactions

$$\mathrm{RHCO} + h\nu = \mathrm{RHCO}' \quad (6)$$

$$\mathrm{RHCO}' + \mathrm{RHCO} = (\mathrm{RHCO})_2, \text{ etc.} \quad (7)$$

$$\mathrm{RHCO}' = \mathrm{RHCO} + \text{energy (fluorescence)} \quad (8)$$

This postulate explains the high polymerization yield at 3130 Å., the existence of fluorescence, and the effects of pressure on polymerization. The drop in polymerization rate between 3130 and 3020 Å. would then be due to a weakening of the bands and a strengthening of the continuum between these two wave lengths. The same postulate does not explain the increase in polymerization quantum yield at still shorter wave lengths. Since the mechanism in reactions 1 to 4 permits of no chain formation, a maximum value of unity is placed on the quantum yield of decomposition. At 2537 Å. the decomposition yield has reached this maximum value, and fluorescence has disappeared, yet polymerization is still produced with an apparent quantum yield of 0.75.

This may only be explained by assuming that the free radicals resulting from the primary dissociation (reaction 1) can produce polymerization in other aldehyde molecules, possibly through the formation of intermediate addition compounds, before combining to give the final decomposition products. Until more evidence is available the authors wish to refrain from undue speculation in this direction.

[13] In view of the number of vibrational degrees of freedom and consequent close spacing of the vibrational energy levels in these molecules, together with the finite width of the energy levels when the total vibrational energy is equal to the energy of dissociation, it may be assumed that in the bimolecular association reactions (4 and 5, above) the product molecule may temporarily accommodate any value of energy. These molecules will, therefore, be sufficiently long-lived to make the rates of association, except at pressures lower than were used here, independent of the concentration of the third body, X. See Kassel, THIS JOURNAL, **53**, 2143 (1931), and Pease, *ibid.*, **54**, 1876 (1932).

The marked rise in decomposition at 2537 Å. cannot be due to activation of mercury vapor in the absorption tube, for spectrum photographs show that with the type of high pressure arc used in this study the 2537 Å. resonance line is completely reversed, only the wings and the continuum to the long wave length side, which are not absorbed by cold mercury vapor, being present.

The authors wish to acknowledge their indebtedness to Dr. J. H. C. Smith for many helpful suggestions made during the course of this work.

Summary

1. The first of a series of articles on the photochemical reactions of the aliphatic aldehydes has been presented. The apparatus and method of study has been described and the experimental results given for propionaldehyde.

2. In the region investigated, λ2537 Å. to λ3130 Å., photochemical decomposition and polymerization are independent reactions. The quantum yield of decomposition is independent of pressure, while the quantum yield of apparent polymerization is directly proportional to the pressure.

3. The variation of the quantum yields of both reactions with wave length has been studied.

4. The principal products of decomposition were found to be carbon monoxide and ethane. A small amount of hydrogen also was formed in decomposition.

5. Fluorescence was produced by exposure to all wave lengths down to and including λ2654 Å.

6. Mechanisms for both photochemical reactions have been proposed.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE ANATOMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

DISTRIBUTION OF ACIDS BETWEEN WATER AND SEVERAL IMMISCIBLE SOLVENTS

BY RAYMOND C. ARCHIBALD

RECEIVED APRIL 25, 1932 PUBLISHED AUGUST 5, 1932

Part I. Monocarboxylic Acids

The distribution ratios at 25° of the six straight-chain members of the saturated monocarboxylic acid series from formic acid to caproic acid have been determined between water and the following solvents: ethyl methyl ketone, tertiary amyl alcohol, secondary butyl alcohol, normal butyl alcohol and normal amyl alcohol. Data have also been included from the literature for ratios between ethyl ether and water[1] and between isopropyl

[1] W. U. Behrens, *Z. anal. Chem.*, **69**, 97 (1926).

ether and water.[2] Since the distribution ratios change slightly with the concentration of the acid, the values of the ratios for ethyl ether have been estimated for an acid concentration of about 0.001 *M* in the water layer. The values for isopropyl ether and water were obtained by using weighted means from the three papers cited for an average acid concentration of both layers of about 0.05 *M*. These values of the distribution ratios in water and ethyl ether, and in water and isopropyl ether are included in the table and plot of the original data. The exact concentrations in the ether layers cannot be calculated because the volumes after mixing are not given. Note: The value given for butyric acid by Werkman in his first paper is undoubtedly in error.

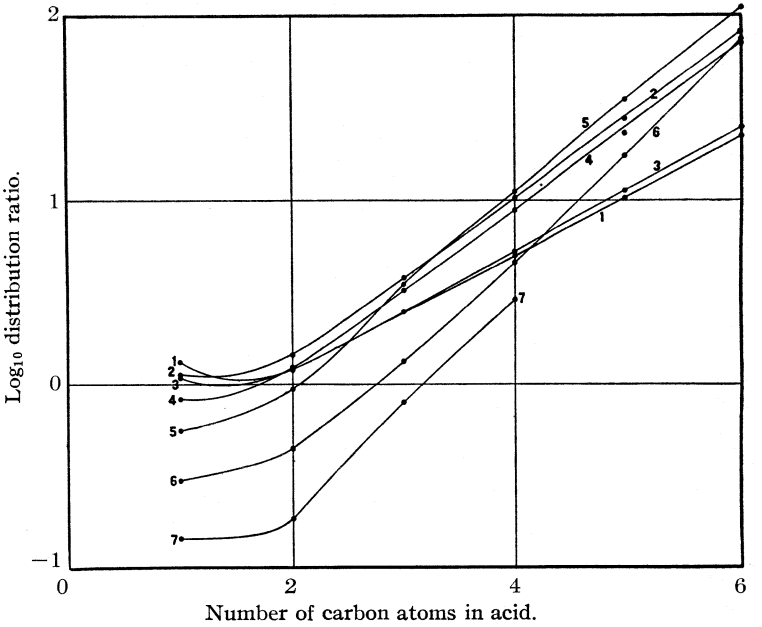


Fig. 1.—Distribution of monocarboxylic acids: 1, ethyl methyl ketone; 2, tertiary amyl alcohol; 3, secondary butyl alcohol; 4, normal butyl alcohol; 5, normal amyl alcohol; 6, ethyl ether; 7, isopropyl ether. Ratios are: moles per liter in solvent layer/moles per liter in water layer.

The plot, Fig. 1, shows the logarithm of the distribution ratio at the concentration given in Table I, or in cases where two concentrations are given, the logarithm of the average distribution ratio.

Experimental

Industrial solvents were obtained from Shell Chemical Company, Sharples Solvents Corporation, Commercial Solvents Corporation, Carbide

[2] C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 302 (1930); O. L. Osburn and C. H. Werkman, *ibid.*, **3**, 264 (1931); C. H. Werkman and O. L. Osburn, *ibid.*, **3**, 387 (1931).

and Carbon Chemicals Corporation, etc. Some were first washed with 20 normal aqueous sodium hydroxide and all were of the highest purity, having been distilled in a 20-foot (6.09 m.) fractionating column described

TABLE I

DISTRIBUTION RATIOS OF MONOCARBOXYLIC ACIDS

Concentrations in millimoles per liter

Acid	Concn. H_2O layer	Concn. solv. layer	Ratio	Av. ratio
	Ethyl Methyl Ketone and Water			
Formic	122.69	165.11	1.3457	1.320
Formic	342.52	443.32	1.2942	
Acetic	148.26	178.66	1.2050	1.193
Acetic	460.45	543.51	1.1804	
Propionic	76.45	189.50	2.4787	2.4787
Butyric	32.78	166.44	5.0774	5.045
Butyric	122.88	615.99	5.0129	
Valeric	31.57	322.36	10.211	10.211
Caproic	13.43	298.89	22.260	22.260
	Tertiary Amyl Alcohol and Water			
Formic	114.43	130.15	1.1373	1.119
Formic	360.56	397.05	1.1012	
Acetic	132.05	195.31	1.4791	1.445
Acetic	374.27	528.29	1.4115	
Propionic	52.01	198.29	3.8125	3.8125
Butyric	16.01	166.97	10.367	10.29
Butyric	52.32	535.05	10.226	
Valeric	11.97	330.74	27.631	27.631
Caproic	3.55	291.72	82.17	82.17
	Secondary Butyl Alcohol and Water			
Formic	118.30	127.81	1.0804	1.074
Formic	346.25	369.53	1.0672	
Acetic	151.00	192.12	1.2723	1.206
Acetic	466.70	531.82	1.1395	
Propionic	72.21	178.46	2.4714	2.4714
Butyric	31.25	159.63	5.1082	5.289
Butyric	91.22	498.96	5.4699	
Valeric	27.42	311.39	11.356	11.356
Caproic	11.65	288.61	24.773	24.773
	Normal Butyl Alcohol and Water			
Formic	256.22	225.07	0.8486	0.829
Formic	784.93	635.54	.8097	
Acetic	150.72	187.57	1.2445	1.232
Acetic	420.54	513.07	1.2200	
Propionic	57.62	186.20	3.2315	3.2315
Butyric	21.09	187.61	8.8957	8.814
Butyric	57.66	503.50	8.7322	
Valeric	13.71	315.50	23.012	23.01
Caproic	4.03	287.40	71.32	71.3

TABLE I (*Concluded*)

Acid	Concn. H_2O layer	Concn. solv. layer	Ratio	Av. ratio
Normal Amyl Alcohol and Water				
Formic	143.86	83.18	0.5782	0.549
Formic	489.89	254.72	.5200	
Acetic	164.51	153.05	.9303	.935
Acetic	488.28	458.64	.9393	
Propionic	53.34	186.00	3.4871	3.4871
Butyric	15.52	173.38	11.171	11.15
Butyric	46.67	519.12	11.123	
Valeric	8.83	312.88	35.43	35.43
Caproic	2.60	284.26	109.3	109.3
Ethyl Ether and Water				
Formic			0.30	
Acetic			.44	
Propionic			1.34	(*Cf.* Ref 1)
Butyric			4.6	
Valeric			17.5	
Caproic			75	
Isopropyl Ether and Water				
Formic			0.145	
Acetic			.184	
Propionic			.810	(*Cf.* Ref. 2)
Butyric			2.90	

elsewhere.[3] Blank titrations were made on all solvents in equilibrium with distilled water at 25°. These titrations showed no appreciable acid in either the water or any of the solvents. The acids used were high grade commercial C. P. products.

The solvent, water and acid were mixed in a flask and allowed to remain, with frequent shaking, in a thermostat at 25.00 ± .01° for several hours. Samples of each layer were pipetted out and titrated in duplicate against standardized 0.1 *N* sodium hydroxide with phenolphthalein indicator. These samples were 25 cc. in all cases except the higher concentrations of formic, acetic and butyric acids, for which 10-cc. samples were used. The values in Table I were obtained from the average of the duplicate titrations. The close check of the duplicate titrations showed that equilibrium had been attained.

Discussion

This work was undertaken for its bearing on the possibility of separating sterols from vitamins by forming some ester of the sterol, such as the gluconate, which might be slightly soluble in water, and fractionating the mixture in a column which gives multiple distribution between two immiscible solvents. The construction and use of this column will be pub-

[3] Evans, Cornish, Lepkovsky, Archibald and Feskov, *Ind. Eng. Chem., Anal. Ed.*, **2**, 339 (1930).

lished later in a paper from this Laboratory dealing with the isolation of the fat-soluble vitamins.

This work is also of interest in connection with the Dakin process for separating amino acids.[4] This process consists in extracting a water solution of the mixed amino acids with normal butyl alcohol or other solvent. The strongly ionized amino acids remain in the water layer, while the slightly ionized acids are extracted. A similar process is also being used in this Laboratory in an attempt to isolate some of the water-soluble vitamins.

Part II. Inorganic Acids

This part of the paper will consider the distribution of hydrochloric, nitric, sulfuric and perchloric acid between water and some of the non-

TABLE II

DISTRIBUTION OF INORGANIC ACIDS

Concentrations in equivalents per liter, except aniline values, which are moles per 1000 g. of solution.

Acid	Concn. solv. layer	Concn. H_2O layer
Solvent: *n*-Butyl Alcohol		
HCl	0.0105	0.0839
HCl	.0857	.4197
HCl	.7586	1.7973
HNO_3	.0208	0.0856
HNO_3	.1455	.3657
HNO_3	.9841	1.5481
H_2SO_4	.0056	0.0937
H_2SO_4	.0387	.4745
H_2SO_4	.3412	2.3416
$HClO_4$	.0353	0.0774
$HClO_4$	.2088	.3224
$HClO_4$	1.1271	1.4065
Solvent: *n*-Amyl Alcohol		
HCl	0.0026	0.0929
HCl	.0279	.4836
HCl	.4213	2.1964
HNO_3	.0071	0.0974
HNO_3	.0829	.4794
HNO_3	.7021	1.8708
H_2SO_4	.0018	0.1007
H_2SO_4	.0059	.5052
H_2SO_4	.0787	2.4714
Solvent: *Tert.*-amyl Alcohol		
HCl	0.0109	0.0956
HCl	.1010	0.4385
HCl	.9616	1.7882
H_2SO_4	.0056	0.0984
H_2SO_4	.0464	.4923
H_2SO_4	.4969	2.2337
Solvent: Methyl Ethyl Ketone		
HCl	0.0024	0.0695
HCl	.0117	.3438
HCl	.1497	1.3749
HNO_3	.0088	0.0647
HNO_3	.0935	.2871
HNO_3	Miscible	
Solvent: Ethyl Ether		
HNO_3	0.0011	0.0847
HNO_3	.0165	.4326
HNO_3	.4263	1.9071
Solvent: Aniline (*Cf.* Ref. 5)		
HCl	0.00599	0.1110
HCl	.01939	.2039
HCl	.04190	.2892
HCl	.04886	.3117
HCl	.05758	.3361
HCl	.09151	.4240
HCl	.1134	.4594
HCl	.1816	.5514
HCl	.3371	.7126
HCl	.8558	1.0247
HCl	1.1299	1.1622
HCl	1.1876	1.1832
HCl	1.446	1.3320
HCl	1.578	1.578

[4] H. Dakin, *Biochem. J.*, **12**, 290 (1918).

aqueous solvents used in Part I. Distributions of these acids were determined in three concentrations, the average concentration for both layers being about 0.05, 0.25 and 1.25 *N*. The layers were approximately equal in volume.

The experimental method is identical with that used for the monocarboxylic acids; 25-cc. samples were used in the two lower concentrations and 10-cc. samples in the highest.

The data on hydrochloric acid in aniline are due to Sidgwick, Pickford and Wilsdon.[5]

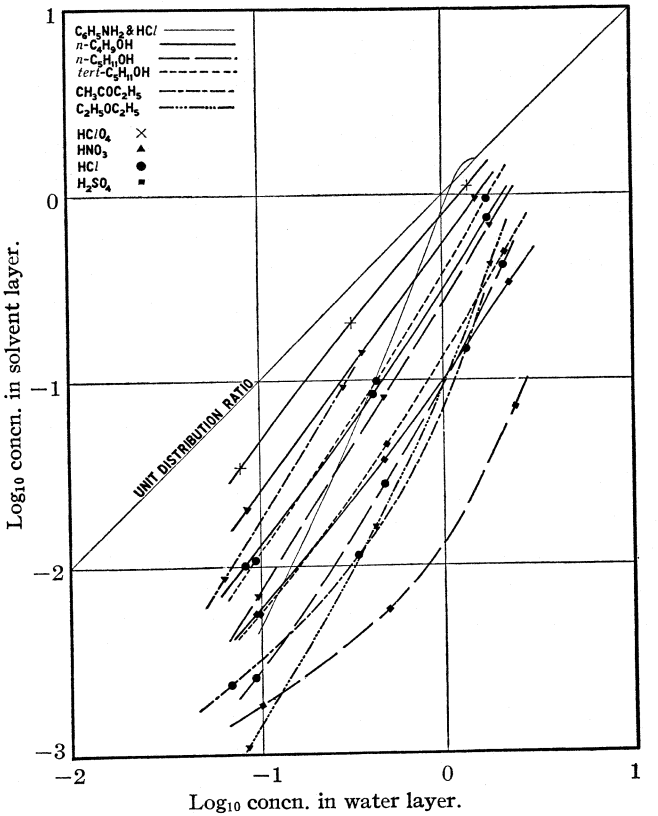


Fig. 2.—Distribution of inorganic acids. Concentrations are in equivalents per liter, except aniline values where hydrochloric acid is in moles per 1000 g. of solution.

Table II shows the acid concentration in the water layer, and in the solvent layer in equilibrium with it. All measurements are at 25.00 ± .01°.

In Fig. 2 the logarithm of the acid concentration in the aqueous layer is plotted against the logarithm of the acid concentration in the solvent layer.

[5] N. V. Sidgwick, P. Pickford and B. H. Wilsdon, *J. Chem. Soc.*, **99**, 1122 (1911).

Discussion

The tendency is for the curves to approach the line denoting unit distribution ratio as the acid concentration is increased. They reach this line at the point where complete miscibility between the two layers occurs, which in the case of nitric acid in ethyl methyl ketone and water is within the range of concentrations studied. The curves may cross this line before the point of complete miscibility, returning to it later, as in the case of aniline and hydrochloric acid.

The curve for hydrochloric acid in aniline and water has a slope of about 2 over most of its length. That is, the concentration of the hydrochloric acid in the aniline layer varies approximately as the square of the acid concentration in the water layer. From this fact it may be assumed that the hydrochloric acid is practically un-ionized in the aniline layer. This condition is approximated also in the curve representing nitric acid in ethyl ether and water. The other curves, however, apparently show more tendency for the acids to be ionized in the non-aqueous layers.

Distribution measurements were also attempted for hydrochloric acid between ethyl ether and water. However, due to the extreme insolubility of hydrochloric acid in ether at all the concentrations studied, it was impossible to make any accurate measurements without a much more refined procedure.

In any one solvent the order of the curves from the line of unit distribution ratio is $HClO_4$, HNO_3, HCl, H_2SO_4, which follows the Hofmeister series for the precipitation of proteins, the sulfate ion being the most efficient. The series is also the same as that found by Randall and Failey[6] for the salting-out effect, rather than the strength of acids series[7] which gives the order HNO_3, HCl, H_2SO_4, $HClO_4$, where perchloric is the strongest acid.

An attempt was made to measure the distribution of hydrochloric acid between propylene oxide and water, but due to the rapid reaction of propylene oxide with hydrochloric acid[8] even in cold dilute aqueous solution, these measurements were impossible. Propylene oxide is more reactive than propylene glycol and consequently much more reactive than ethers such as ethyl ether. This extreme reactivity is probably due to the fact that the oxygen atom is one member of a three-membered ring, and this makes propylene oxide more suitable as a reagent than a solvent.

The purpose of this research was to determine quantitatively which acid would be most suitable for acidifying a water solution, one component of

[6] Randall and Failey, *Chem. Rev.*, **4**, 285 (1927); *ibid.*, **4**, 271 (1927); *ibid.*, **4**, 291 (1927).

[7] Hantzsch and Voigt, *Ber.*, **62B**, 975–984 (1929); Hantzsch and Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932); Hall, *The Nucleus*, **6**, 87–88, 91 (1929).

[8] Henry, *Bull. acad. roy. Belg.*, p. 397 (1903); Michael, *Ber.*, **39**, 2786 (1906); Smith, *Z. physik. Chem.*, **93**, 59 (1919); Markownikoff, *Compt. rend.*, **81**, 799 (1875); Nef, *Ann.* **335**, 205 (1904).

which was to be extracted out with one of the solvents mentioned above. Since it was necessary to extract with very large amounts of solvent, many times it was imperative that the acid be very insoluble in the solvent in order that the solution remain acid until the end of the extraction process.

Acknowledgment.—The author acknowledges his indebtedness to Dr. Herbert M. Evans and to Dr. R. E. Cornish of this Department for their valuable assistance and advice.

Summary

Distribution ratios of six fatty acids and four inorganic acids were measured between water and several solvents which are not miscible with water. A short discussion of the results is given.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE KINETICS OF GAS EXPLOSIONS. III. THE INFLUENCE OF HYDROGEN ON THE THERMAL DECOMPOSITION OF OZONE SENSITIZED BY BROMINE VAPOR, AND THE DETERMINATION OF THE EXPLOSION TEMPERATURE[1]

BY W. FEITKNECHT[2] AND BERNARD LEWIS[3]

RECEIVED APRIL 25, 1932 PUBLISHED AUGUST 5, 1932

In a previous paper[4] it was shown that inert gases exert a small influence on the rate of decomposition of ozone in the presence of bromine as long as the ozone pressure is low. At higher pressures the rate is slowed down and the explosion pressure limit of ozone is increased considerably. The efficiency of inert gases in increasing the explosion limit decreases with increasing molecular weight.

The influence of hydrogen was not included in the previous investigations. It seemed of special interest, as hydrogen increases considerably the photochemical rate of decomposition of ozone with the simultaneous formation of water.[5] Belton, Griffith and McKeown[6] found a similar influence of hydrogen on the thermal decomposition of ozone, whereas Schumacher[7] states that hydrogen has only a slight effect on the thermal

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Formerly Foreign Exchange Fellow, University of Pittsburgh.

[3] Physical Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[4] Part I, THIS JOURNAL, **53**, 2910 (1931). Part II, *ibid.*, **54**, 1784 (1932).

[5] Weigert and Böhm, *Z. physik. Chem.*, **90**, 189 (1915); Griffith and Shutt, *J. Chem. Soc.*, **123**, 2752 (1923).

[6] Belton, Griffith and McKeown, *ibid.*, **126**, 3153 (1926).

[7] Schumacher, THIS JOURNAL, **52**, 2388 (1930).

decomposition. It has been found by one of us[8] that ozone is indeed extremely stable in the presence of hydrogen at room temperatures. However, at higher temperatures (80 to 90°), the influence of hydrogen is so great that under certain conditions the ozone may be made to explode violently. The thermal decomposition of ozone sensitized by bromine vapor, at temperatures (<15°) at which the solid oxide of bromine is formed, is unaffected by hydrogen.[9]

The present experiments with ozone–bromine mixtures and hydrogen were carried out in the same way as those with similar mixtures and inert gases described previously.[4] The experimental temperature employed was 25°. The rate of the non-explosive reaction was of the same order as that for corresponding mixtures with other inert gases, and the reaction went to about 70% completion in ten minutes. This strongly indicated that no water was formed, for water in very small amounts (<0.1 mm.) poisons the walls and decreases the rate of decomposition of ozone materially.[4]

A more direct method was employed to detect water formation, if any. A mixture, the original composition of which was 50 mm. ozone, 20 mm. hydrogen and 0.5 mm. bromine, was cooled down to −65° after 87% of the ozone had decomposed. The vessel was evacuated removing all gases except water (if formed) and then warmed up again to 25°. No pressure increase could be detected, although the manometer employed read easily to less than 0.1 mm., indicating that less than 0.5% of the hydrogen could have been transformed to water.

These results do not conflict with the chain mechanism suggested by the authors, for the explanation of the decomposition of ozone sensitized by bromine in which the oxygen atom is an important link, for according to the experiments of Harteck and Kopsch,[10] oxygen atoms do not react readily with hydrogen molecules. The results indicate that the second carrier in the proposed chain, namely, an energy-rich oxygen molecule, also does not react with hydrogen to form water at the temperature of these experiments.

Whenever the ozone concentration was above the explosion limit, the hydrogen was burned to water in the explosion. If the vessel was then evacuated in the usual way, it proved to be very inactive in the next experiment. It was shown previously[4] that the direct introduction of a small amount of water vapor affected the vessel in a similar way. The vessel could be reactivated only after prolonged evacuation accompanied by heating and subjecting the vessel to sparking with a high-tension coil. This was in striking contrast to the unaltered activity

[8] Lewis, forthcoming contribution.

[9] Lewis and Schumacher, *Z. physik. Chem.*, **6B**, 423 (1930).

[10] Harteck and Kopsch, *ibid.*, **12B**, 327 (1931).

of the vessel after a non-explosive reaction, a further proof that in the latter case no water is formed.

The explosion limit of ozone (sensitized by bromine) was found to be greatly increased by hydrogen. It was nearly twice as high as for a similar mixture in which the hydrogen is replaced by helium. Hydrogen, therefore, fits well into the order in which inert gases increase the explosion limit—namely, argon, oxygen, nitrogen, helium and hydrogen.

The final pressure after an explosion was always considerably lower than the pressure calculated on the assumption that all the hydrogen had oxidized to water and all the ozone had decomposed to oxygen. On alternately raising and lowering the temperature of the products, the deviation in pressure from Gay-Lussac's law was such as to indicate that some liquid had condensed on the wall of the vessel at 25°. The experiments could be reproduced very well. The difference between the calculated and observed pressures increased with increasing amounts of bromine and hydrogen but were affected little by changes in the ozone pressure, as can be seen from Table I.

TABLE I

PRESSURE CHANGES IN EXPLOSIONS OF OZONE–BROMINE–HYDROGEN MIXTURES AT 25°

a, expected total pressure after explosion on basis of 100% of water formation; *b*, total pressure observed after explosion.

Expt.	Vessel	O_3, mm.	H_2, mm.	Br_2, mm.	*a*	*b*	*a* − *b*
72–11	Glass	40	10	1	66	65.4	0.6
75–3	Quartz	40	10	1	66	65.2	0.8
72–7	Glass	40	10	5	70	67.0	3.0
72–8	Glass	40	10	5	70	67.2	2.8
74–3	Glass	40	10	10	75	70.3	4.7
74–6	Glass	40	10	10	75	70.3	4.7
75–1	Quartz	40	10	10	75	70.1	4.5
75–7	Quartz	40	10	10	75	70.1	4.5
75–9	Quartz	60	5	10	102.5	101.3	1.2
75–7a	Quartz	60	10	10	105	99.8	5.2
75–10	Quartz	60	15	10	107.5	98.2	9.3
75–8	Quartz	60	10	20	115	108.5	6.5
75–11	Quartz	60	15	20	117.5	106.1	11.4

In the first column, the first numbers represent the experimental series, and the numbers after the dash the experiment in the series.

These results can only be due to the formation of hydrogen bromide in the explosion,[11] forming afterward with water a solution with low vapor pressure. To prove this the products of several successive explosions were condensed in a side tube and analyzed. The solution proved to be fairly concentrated in hydrogen bromide.

[11] If any hydrogen bromide were formed in the non-explosive reaction it would have reacted with ozone immediately to give water, oxygen and bromine (see Lewis and Feitknecht, THIS JOURNAL, **53**, 3565 (1931); *ibid.*, **54**, 1784 (1932)).

The excellent reproducibility and the way in which the amount of hydrogen bromide formed depends upon the initial pressures of bromine, hydrogen and ozone, suggest that the following equilibrium is established in the explosion.

$$2H_2O + 2Br_2 \rightleftharpoons 4HBr + O_2 \qquad (1)$$

If the amounts of hydrogen bromide and water formed were known, the equilibrium constants calculated from these data could be compared with the equilibrium constants of this reaction at different temperatures derived from independent sources, and an estimate could be obtained of the temperature reached in these low-pressure explosions.

Determination of the Explosion Temperature from the Equilibrium Attained.—Owing to the condensation of hydrogen bromide and water in the lead tube, the use of a simple manometric method of determining the equilibrium was precluded.

TABLE II

ESTIMATED COMPOSITIONS OF MIXTURES IN MM. AFTER EXPLOSION AND EXPERIMENTAL EQUILIBRIUM CONSTANTS OF REACTION (1)

Expt.	H_2O	Br_2	O_2	HBr	$P_{calcd.}$	$P_{obs.}$	$(H_2O + HBr)$ $-(P_{calcd.} - P_{obs.})$	$K_{calcd.}$	$K_{corr.}$
74–3	9	9	55.5	2	75.5	70.3	5.8	5.61×10^3	1×10^3
75–7a	9	9	85.5	2	105.5	99.8	5.3	3.64×10^3	6.6×10^2
75–8	8.5	18.5	85.75	3	115.75	108.5	4.25	2.71×10^3	4.9×10^2
75–10	13.5	8.5	83.25	3	108.25	98.2	6.45	1.49×10^3	2.7×10^2
75–11	13.0	18.0	83.5	4	118.5	106.1	4.6	1.95×10^3	3.5×10^2

The total amount of hydrogen bromide formed in the explosion (Table II, Column 5) could be estimated by a method of trial and error. First a value is assumed and, together with the original pressures of hydrogen, bromine and oxygen (Table I), the total amounts of water, bromine and oxygen are calculated (Columns 2, 3 and 4). Thus the total pressure, $P_{calcd.}$ in Column 6, is known. Column 7 contains the observed pressure. $P_{calcd.} - P_{obs.}$ equals the amount of water and hydrogen bromide condensed out; and since Columns 2 + 5 give the total amount of these products formed, Column 8 represents the pressure of water and hydrogen bromide in the gas phase. Several such values in Column 8 are calculated for different assumed values of hydrogen bromide in Column 5. These vapor pressures are compared with the data of Wrewsky, Sawaritzky and Scharloff[12] on the vapor pressure and composition of the vapor above solutions of hydrogen bromide in water. It turns out that in experiments with 10 millimeters and more of hydrogen and bromine the mixture must correspond approximately to the one having the smallest vapor pressure, or one in which the composition of the liquid and gas phases is identical—in other words, to a mixture with approximately 20 mole per cent. of hydrogen bromide. The final values of hydrogen bromide thus

[12] Wrewsky, Sawaritzky and Scharloff, *Z. physik. Chem.*, **112**, 97 (1924).

estimated are given in Column 5, Table II, and the corresponding vapor pressure of hydrogen bromide plus water at 25° in Column 8. For experiments 75–8 and 75–11 the values in Column 8 are about 1 mm. lower than those which would correspond to the minimum vapor pressure of the hydrogen bromide–water solution. This is partly due to the errors which may accumulate by the addition and subtraction of several somewhat uncertain values and to the solution of a small amount of bromine in these particular experiments with higher bromine concentrations. In general the error in the hydrogen bromide values given is about ±0.5 mm. This is sufficiently accurate for our purpose as it introduces an error of only about ±4.5% in the final explosion temperature.

By substituting the pressures of water, bromine, hydrogen bromide and oxygen in atmospheres in the formula

$$K = \frac{[H_2O]^2\,[Br_2]^2}{[HBr]^4\,[O_2]} \qquad (2)$$

the experimental equilibrium constant K can be determined for the different experiments. There is not much variation of the constants in Column 9, Table II. The differences observed are attributable to differences in the temperatures at which the equilibria are frozen out in the different experiments. However, the error in the estimation of hydrogen bromide would introduce about the same differences, so that it is not possible to draw definite conclusions on this point. These K's are calculated for the gas pressure at the temperature 298° K. It will be seen later that the temperature at which the equilibrium is established is approximately 5.5 times higher. The K's should therefore be corrected for the pressures existing at this temperature, and from formula (2) it follows that they should be divided by 5.5. The corrected constants are given in the last column of Table II.

There are two methods by which the equilibrium constant K of formula (2) can be approximately calculated theoretically.

1. By using the Nernst formula:[13]

$$\log K = -\frac{Q}{4.57\,T} + \Sigma v\ 1.75 \log T + \Sigma v C \qquad (3)$$

On introducing the values given by Nernst for the conventional constants C and Σv and the value of Q as the difference between the heats of formation of $2H_2O$ and 4HBr (that is, $-115{,}600 + 48{,}400 = -67{,}200$), equation 3 becomes

$$\log K = +\frac{14{,}700}{T} - 1.75 \log T - 0.6 \qquad (4)$$

The values for K thus calculated are given in the fifth column of Table III as K_1, for temperatures between 1500 and 2000° A.

[13] Nernst, "Die theoret. u. experimentellen Grundlagen des neuen Wärmesatzes," 1918, p. 112.

TABLE III

CALCULATED EQUILIBRIUM CONSTANTS OF REACTION (1) AT DIFFERENT TEMPERATURES

T, °A.	K_{HBr}	K_{H_2O}	$K_2 = \frac{(K_{HBr})^2}{K_{H_2O}}$	K_1
1500	3.66×10^{-5}	5.02×10^{-12}	2.67×10^{2}	4.36×10^{3}
1600	6.10×10^{-5}	6.34×10^{-11}	5.87×10^{1}	9.60×10^{2}
1700	9.9×10^{-5}	5.7×10^{-10}	1.72×10^{1}	2.45×10^{2}
1800	1.51×10^{-4}	4.26×10^{-9}	0.53×10^{1}	7.41×10^{1}
1900	2.19×10^{-4}	2.4×10^{-8}	$.20 \times 10^{1}$	2.51×10^{1}
2000	3.11×10^{-4}	1.17×10^{-7}	.83	0.93×10^{1}

2. The second method is derived from the fact that

$$K = \frac{[H_2O]^2\,[Br_2]^2}{[HBr]^4\,[O_2]} = \frac{K^2_{HBr}}{K_{H_2O}} \qquad (5)$$

K can therefore be calculated from the constants of the hydrogen bromide and water equilibria, namely

$$2\,HBr \rightleftharpoons H_2 + Br_2 \qquad (6)$$

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2 \qquad (7)$$

Vogel von Falckenstein[14] has shown experimentally that the hydrogen bromide equilibrium follows the formula of Nernst[15] fairly well, namely

$$\log K_{HBr} = -\frac{5223}{T} + 0.553 \log T - 2.72 \qquad (8)$$

The K for the water equilibrium was calculated from the formula given by Lewis and Friauf[16]

$$\log K_a = +\frac{57{,}295}{4.57T} - 0.848 \log T - 1.474 \times 10^{-4}\,T + 7.78 \times 10^{-8}T^2 - 8.72 \times 10^{-12}T^3 + 0.0616 \qquad (9)$$

It should be mentioned that K_a calculated from this formula is $K_a = [H_2O]/[H_2]\,[O_2]^{1/2}$, while the K_{H_2O} to be used in (5) is

$$K_{H_2O} = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$

Therefore

$$K_{H_2O} = 1/K_a^2 \qquad (10)$$

Columns 2 and 3, Table III, contain these values of K_{HBr} and K_{H_2O} and Column 4 contains K_2, the desired constant by the second method—namely, $K_2 = K^2_{HBr}/K_{H_2O}$.

It is seen that K_1 is roughly one order of magnitude larger than K_2, corresponding to an average temperature difference of 200°. This is roughly of the same order as the uncertainty in temperature arising from the uncertainty in the value of the hydrogen bromide formed.

Comparing K_1 and K_2 with the $K_{corr.}$ of Table II, one observes that the equilibrium constants found correspond to a temperature of about 1600 ± 100°A. This temperature is probably not the maximum explosion

[14] Von Falckenstein, *Z. physik. Chem.*, **68**, 270 (1909); **72**, 113 (1910).

[15] Nernst, *Z. Elektrochem.*, **18**, 687 (1909).

[16] Lewis and Friauf, THIS JOURNAL, **52**, 3905 (1930).

temperature which is possible in the mixtures considered because the experiments were not carried out adiabatically, but is indicative of the temperature at which the equilibria found were frozen out.

Summary

The influence of hydrogen on the thermal decomposition of ozone sensitized by bromine vapor has been investigated. In the non-explosive reaction it is found that hydrogen behaves only as an inert gas retarding the reaction to about the same degree as other inert gases do. No water is formed, indicating that hydrogen does not react readily at room temperature with the oxygen atoms and energy-rich oxygen molecules assumed to play a role in the decomposition of ozone. The explosion pressure limit of ozone is greatly increased by hydrogen, which fits well into the order in which inert gases increase the explosion limit—namely, argon, oxygen, nitrogen, helium and hydrogen. During the explosion the hydrogen is burned to water and the following equilibrium is established

$$2H_2O + 2Br_2 \rightleftharpoons 4HBr + O_2$$

The concentrations of the products are determined and the equilibrium constants calculated. These are compared with the equilibrium constants at different temperatures derived from two independent sources. The temperature at which the equilibria are established is found to be 1600 $\pm$ 100° Absolute.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

STERIC HINDRANCE AND COLLISION DIAMETERS[1]

BY HENRY EYRING

RECEIVED APRIL 25, 1932 PUBLISHED AUGUST 5, 1932

Introduction

A large part of chemistry is interpretable in terms of potential energy diagrams. Stable compounds are configurations of low potential energy which are separated from configurations of still lower energy by energy ridges of approximately 20 kg. cal. or more per mole. If the ridge is much lower than this the rate at which molecules accumulate sufficient energy to pass over the barrier, even at ordinary temperatures, make it impossible to isolate any but the molecular species of lowest energy. Energy barriers are sometimes lowered by two molecules colliding, making a complex from which a new species emerges—a bimolecular reaction. A rearrangement or splitting inside a single molecule is a unimolecular

[1] Presented except for minor changes September 2, 1931, as part of the symposium on the Kinetics of Chemical Reactions at the Buffalo meeting of the American Chemical Society, by Henry Eyring and J. C. Slater.

reaction. Every bimolecular reaction has a unimolecular stage, *i. e.*, the rearrangement inside the complex.

Spectroscopy gives the information from which potential energy curves for diatomic molecules can be constructed. A convenient way of doing this is to use Morse curves.[2]

Quantum mechanics and the Pauli principle give approximate values for the potential energy of a complex configuration of atoms in terms of the potential energies that would exist between pairs of electrons if the other electrons were not present. Thus for reactions involving three and four valence electrons it is possible to construct potential energy functions such that the minimum energy which permits molecules to approach near enough to exchange partners can be calculated.[3]

Calculation of Potential Energy of Molecules.—In a recent paper by Slater,[4] the method of calculating energy terms in complex atomic spectra has been extended to molecules. For a definite way of drawing the valence bonds in molecules perturbation theory gives

$$E = Q + \Sigma\alpha_p - {}^1/_2\Sigma\alpha_u \qquad (1)$$

Here Q is the sum of all coulombic interactions plus the sum of the energies due to mutual polarization of atom pairs (van der Waals forces) plus terms arising from permanent dipoles. $\Sigma\alpha_p$ is the sum of the resonance attraction between the pairs forming shared electron bonds. ${}^1/_2\Sigma\alpha_u$ is the sum of the resonance repulsions between all pairs where there is not a bond and can be evaluated in exactly the same way as the terms, α_p, that is, as half the interchange bond that exists between the electrons when paired. In these considerations it is immaterial how the valence electrons are distributed among the various atoms, that is, whether we are considering monovalent or polyvalent atoms. Electron pair bonds within atoms are the same things as closed shells, and are formed inside all atoms showing less than the highest spin valence. For purposes of calculations these bonds need not be considered different in kind from those between neighboring atoms. The interchange integrals for these internal bonds correspond to half the difference between definite terms of successive multiplicities in the atom, and are known from atomic spectra.

Equation (1) is a general result, as may be seen in the following way. Consider any system of molecules, such that all valence electrons are bound in definite electron pairs. Then an approximate wave function can be set up, corresponding to this way of drawing the electron bonds. And the energy value connected with this wave function is just analogous to the expression (1).

[2] Morse, *Phys. Rev.*, **34**, 57 (1929).

[3] Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931); Eyring, THIS JOURNAL, **53**, 2537 (1931).

[4] Slater, *Phys. Rev.*, **38**, 1109 (1931).

The way of setting up a wave function corresponding to definite bonds is interesting. Suppose the $2n$ valence electrons are distributed among $2n$ states whose wave functions have the dependence on coördinates given by $a, b, c, d, \ldots$, and suppose the bonds are situated between states as indicated by the lines, a-b, c-d, e-f, ..., etc., where more than one electronic function can belong to the same atom. Now to specify a state of the system completely we must give not only the dependence on coordinates but also on spin. Thus if α represents a spin directed along a fixed axis, β a spin in the opposite direction, such a state is given by assigning to each function $a, b, \ldots$, a definite spin, as is given by the symbol $(a\alpha)\ (b\beta)\ (c\alpha)\ (d\beta)\ (e\alpha)\ldots$. To get the actual wave function, we must form an antisymmetric function of the electrons, in a manner which has been described elsewhere. This state which we have symbolized above does not correspond to valence binding; we require rather a linear combination of such states. This linear combination is of the following nature. In each state concerned in it, the two electrons in a pair, as a and b, have opposite spins, but in some the spins are arranged $\alpha\beta$, in others $\beta\alpha$. There are, in other words, just 2^n different states consistent with this condition, and all of them are added together to get the required linear combination. The coefficient multiplying the functions for each state is $+1$ if an even number of interchanges of spins is required to get back to the original function and -1 if an odd number of interchanges is required.

We should consider the relation of this procedure to the case of a chemical reaction. Suppose after a reaction the eigenfunction a is paired with c instead of b, and that b simultaneously becomes paired with d. Then a different function representing the new arrangement of bonds is easily found. If by a reaction the bonds change adiabatically from the one state to the other, the perturbation theory gives us a two-rowed secular determinant the lowest root of which gives the energy during reaction. This equation for the energy has the form

$$E = Q + \Sigma\alpha_p - {}^1/_2\Sigma\alpha_u + \sqrt{{}^1/_2((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2)} \quad (2)$$

The quantities not under the radical sign have the significance given the same symbols in equation (1). These quantities outside of the radical do not include the bonds between the four electrons which interchange partners during the reaction. α_1 and α_2 are the bonds between these latter electrons before reaction, β_1 and β_2 the bonds after the reaction and γ_1 and γ_2 bonds which have an appreciable value for configurations intermediate between the initial and final states. These quantities are explained in more detail for equation (3) which is a special case of (2). Equation (2) should be used for reactions involving steric hindrance. Let us now consider the potential arising from the collision of two molecules.

Kinetic Theory Diameters

We shall content ourselves here with an illustrative example. For four monovalent atoms we have the expression for the potential energy

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \sqrt{1/2((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2)} \quad (3)$$

Greek letters are for interchange binding. The italic letters are for the types of binding which are independent of spin, coulombic plus van der Waals, etc. Figure 1 represents molecule WX colliding with molecule ZY. The sum written on the line joining the symbols for two atoms is the total energy required to separate these atoms if the other two atoms were far away. If WX is at a considerable distance from YZ the radical in (3) can be expanded considering $\alpha_1 + \alpha_2$ large compared with $\beta_1 + \beta_2$ and $\gamma_1 + \gamma_2$.

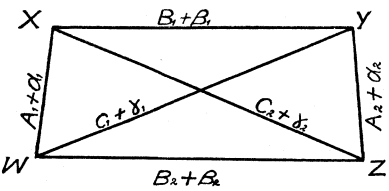


Fig. 1.—Potential terms which determine the total potential of colliding molecules.

This gives

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \alpha_1 + \alpha_2 - 1/2(\beta_1 + \beta_2 + \gamma_1 + \gamma_2) \quad (4)$$

i. e., interchange attraction between the electrons whose spins are antiparallel and a repulsive interchange potential with a coefficient of $1/2$ between all other pairs where there is no chemical bond. Equation (4) may equally well be regarded as a special case of (1). In an ordinary collision there is practically no distortion of the two molecules so that $(A_1 + A_2 + \alpha_1 + \alpha_2)$ stays constant throughout the process. The collision potential is thus

$$E = B_1 + B_2 + C_1 + C_2 - 1/2(\beta_1 + \beta_2 + \gamma_1 + \gamma_2) \quad (5)$$

As an example we will consider the collision of two H_2 molecules. Sugiura's[5] evaluation of Heitler and London's[6] potential energy for an H_2 molecule is used for evaluating the quantities in (5). The curve $f(r)$ in Fig. 2 gives the interchange potential between two H atoms as a function of the distance. This serves to determine β_1, β_2, γ_1 and γ_2. The coulombic parts of B_1, B_2, C_1 and C_2 are determined similarly from the curve $F(r)$. The polarization or van der Waals potential is likewise independent of the spin and can be calculated as the sum of four parts to be added to the coulombic terms. We use $101/r^6$ in kg. cal. for the van der Waals potential between each pair of atoms. r is to be expressed in Ångströms. This is the value London selects.[7] Eisenschitz and London's[8] theoretical value is $91.5/r^6$. This latter value for the van der Waals poten-

[5] Sugiura, *Z. Physik*, **45**, 484 (1927).

[6] Heitler and London, *ibid.*, **44**, 455 (1927).

[7] London, *Z. physik. Chem.*, [B] **11**, 222 (1930).

[8] Eisenschitz and London, *ibid.*, **60**, 491 (1930).

tial would make the theoretical curve agree more closely with the Lennard-Jones curve for large distances between hydrogen molecules but also makes the difference slightly larger when the molecules come closer together.

The resulting total potential energies for various orientations of the H_2 molecules are given as curves I and III of Fig. 3. These are to be compared with the Lennard-Jones[9] empirical potential energy curve II for the collision of two hydrogen molecules. His curve was obtained by choosing the constants A and B and the powers of r in the equation for the potential $E = Ar^{-13\,1/3} - Br^{-4}$ so as to lead to the experimental second virial

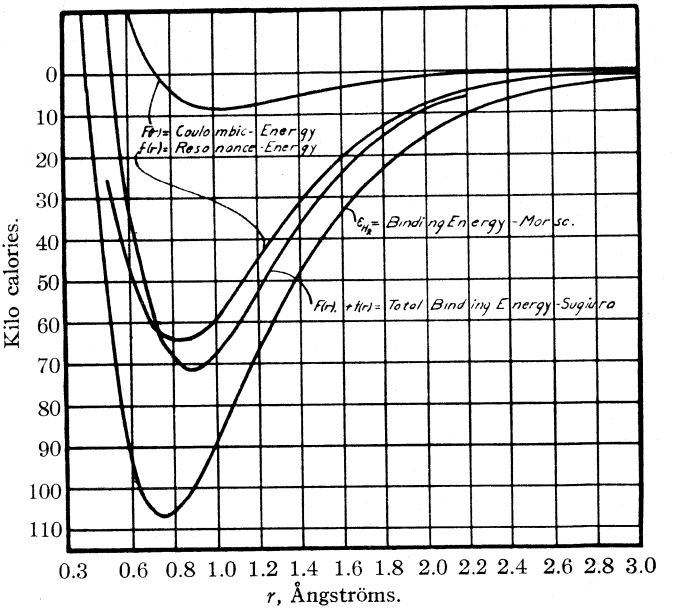


Fig. 2.—Potential energy of the H_2 molecule.

coefficient. The values given are $A = 2.473 \times 10^5$ and $B = 5.65$. In all three curves the abscissa is the distance between the centers of gravity of the colliding molecules. The ordinate is the potential energy referred to zero energy for infinite abscissas. Curve I is for a collision between two molecules colliding with axes parallel to each other but perpendicular to the line joining the centers of gravity of the molecules. As long as the two molecular axes remain perpendicular to the line joining centers of gravity the energy does not change perceptibly (at these large distances) with rotation of one of the molecules about this line. Curve III, however, gives the potential energy for the extreme case in which both molecular axes have turned in such a way that they coincide with the line joining molecular centers of gravity. This gives a much greater repulsion for a

[9] Fowler, "Statistical Mechanics," Cambridge Univ. Press, 1929, Chapt. X.

fixed distance between centers of gravity since it brings two of the colliding atoms much closer together. For comparison with II a weighted average of all configurations should be taken. Both geometrical and energy considerations tend to weight the low lying configurations. The weighted curve of course varies with the temperature but would not differ greatly from I at the temperature for which II represents experiment. The theoretical minimum is 0.05 kg. cal. deeper than the minimum of curve II calculated from experiment. The fact that an oscillator always has a half quanta of energy decreases the discrepancy. Even if the value $91.5/r^6$ is used for calculating van der Waals forces the theoretical minimum is still 0.038 deeper than the minimum of the Lennard-Jones curve. The general agreement is fairly satisfactory and it is probably too early to decide which method of obtaining the potential curve is the better.

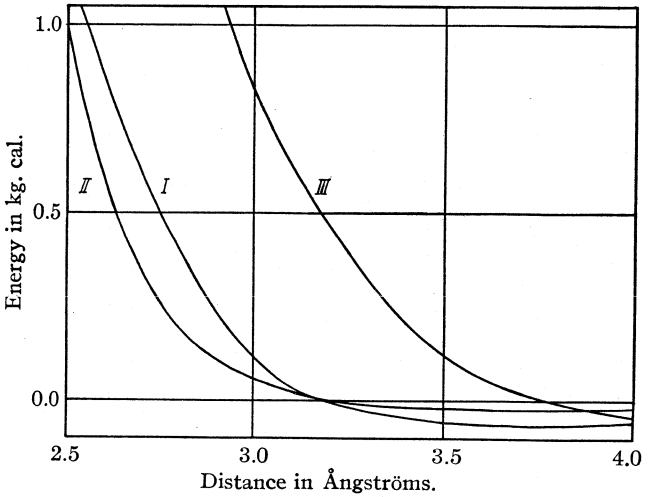


Fig. 3.—Potential energy curve for the collision of two hydrogen molecules.

Cremer and Polanyi[10] have calculated the equilibrium distance between H_2 molecules in the crystal lattice using essentially the method used here for the liquid. They were interested in ascertaining the applicability of the Morse curve for this purpose and so used ϵ_{H_2} of Fig. 2 rather than $f(r)$ for calculating β_1, β_2, γ_1 and γ_2. They neglected coulombic binding. This led to a calculated equilibrium distance between H_2 molecules of 5 Ångströms as compared with an experimental 4 Ångströms. Using the same assumptions in the case of HCl, HBr and HI the agreement was much better, probably indicating that the Morse curve is more satisfactory in these cases. Since the Morse curves are correct in the

[10] Cremer and Polanyi, *Z. physik. Chem.*, [A] Bodenstein Festband, 720 (1931).

neighborhood of the minimum they are probably better for calculating activation energies than for calculating kinetic theory diameters.

Eisenschitz and London[8] have given potential energy curves at large distances for the attraction of two hydrogen atoms in a singlet state and the repulsion in a triplet state. It is of considerable interest in addition to know how two hydrogen atoms interact when they are each bound to another atom since it is this interaction which largely determines the physical properties of the hydrocarbons as well as the properties of hydrogen itself. In Fig. 4 we have drawn the corresponding experimental and theoretical curves. The ordinate of curve I is the van der Waals force,

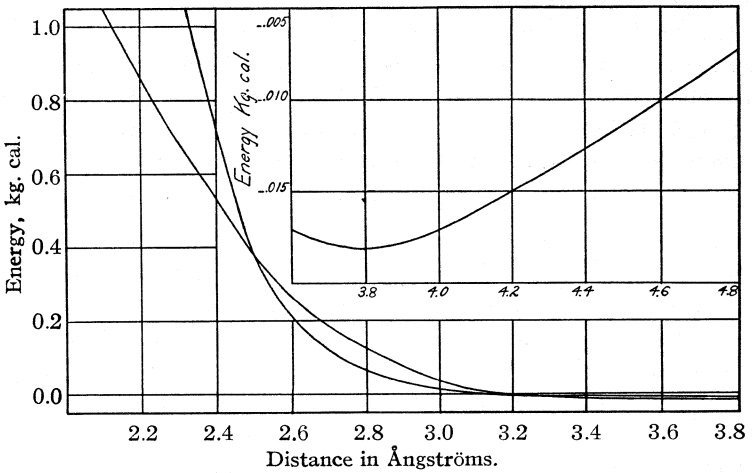


Fig. 4.—Potential energy between widely separated saturated hydrogen atoms.

$101/r^6$, plus the theoretical coulombic integral minus one-half the interchange integral. The ordinate of curve II is one quarter the Lennard-Jones potential between two H_2 molecules plotted, however, against an abscissa which instead of being the distance between centers of gravity of the molecules is the corresponding distance between two H atoms one from each molecule for configurations in which all four such distances are equal. This way of choosing the abscissa is justified by the remarks previously made in connection with Curve I, Fig. 3, that as long as the two molecular axes remain perpendicular to the line joining centers of gravity the energy does not change perceptibly with rotation of one of the molecules about this line. Thus, the statistical curve given by Lennard-Jones gives substantially the potential energy for the configuration assumed. The upper right-hand corner of Fig. 4 simply gives a continuation of Curve I on a larger scale. We shall find such a curve useful in discussing the physical and chemical properties of the hydrocarbons.

All the physical properties of a gas such as the kinetic theory diameter heat of vaporization, compressibility, coefficient of expansion, Sutherland constant and specific heats are deducible from a correct potential energy surface. Conversely these physical properties may be used for determining constants in an equation for the potential energy which in turn gives the activation energy. This fact is of importance in the many cases where the complete quantum mechanical calculations of the energy integrals are excessivly difficult to obtain.

The method used for considering the collision of H_2 molecules may be extended to collisions between polyatomic molecules using Morse curves for the energy between atom pairs, x-ray data for the position of the atoms inside the molecules and substituting in Equation 1. The repulsive potential is simply the sum of one-half the interchange integrals between all pairs of atoms one from each molecule. The coulombic and van der Waals forces are all attractive. The van der Waals forces are calculable either by the method of Slater and Kirkwood[11] or of London.[7]

Steric Hindrance

We may now consider another application of Equations (1) and (2). Since all the interchange integrals are presumably negative the potential energy terms, $-{}^1/_2 \Sigma \alpha u$, increase as unpaired electrons approach each other and are largely responsible for steric hindrance. This repulsion becomes appreciable at kinetic theory diameters as we have just seen and increases exponentially upon closer approach. Permanent dipoles localized in bonds give additional steric effects. The electric moments are known in many cases so that this term is roughly calculable. The other source of attractive potential, van der Waals potential and the coulombic energy are readily calculable.

That the interchange forces are an important factor in steric hindrance is shown in a recent paper by Stuart.[12] He examined the experimental data for heats of combustion of substituted benzene isomers differing only in the relative position of certain radicals. After theoretically calculating the polarization and dipole potentials there is left in many cases a positive potential energy which must be attributed to the repulsive interchange energy between neighboring unpaired electrons. To calculate the energy from potential energy curves for diatomic molecules one must know what fraction of the total energy is coulombic. The coulombic part is 10% of the total in the case of H_2,[13] for Li_2 it is 22%[14] and for Na_2[15] it is 28.3%. It must be estimated in other cases. The rest of the potential energy is

[11] Slater and Kirkwood, *Phys. Rev.*, **37**, 682 (1931).
[12] Stuart, *ibid.*, **38**, 1372 (1931).
[13] Sugiura, *Z. physik. Chem.*, **45**, 484 (1927).
[14] Bartlett and Furry, *Phys. Rev.*, **37**, 1712 (1931).
[15] Rosen, *ibid.*, **38**, 255 (1931).

interchange binding except for the small fraction due to polarization. The percentage of coulombic binding for a particular molecule from the minimum out to almost complete dissociation is constant to about 1% in the cases where it is known.

It is of some interest to estimate the magnitude of steric effects in a typical case. Quantum theoretical considerations[16] lead to the conclusion that the two strongest eigenfunction bonds in an oxygen atom will make an angle of 90° with each other. This angle will be modified by the positive interchange energy $-\alpha/2$ between H atoms, by the negative coulombic energy, the negative van der Waals energy, and the positive energy due to the two dipoles. In addition to these factors there is a new one to consider for directed valences. If one considers the Heitler–London coulombic and interchange integrals for a bond formed from a directed P eigenfunction and a spherically symmetrical one, it is found that the bond energy, E, depends in the following way on the angle, θ, between the axis through the atoms and the axis of the directed eigenfunction.

$$E = L\cos^2\theta + M\sin^2\theta$$

Thus for $\theta = 0$ we have $E = L$, the heat of dissociation of the strongest possible bond. Lacking precise information we shall assume $M = L/5$. We can then construct Table I for the energy terms between the two H atoms in H_2O for angles of 90, 110 and 120° between the OH bonds. The distance O to H is taken as 0.98 Ångströms and the value L for an OH bond is taken as 104 kg. cal.

TABLE I

Angle between bonds	Distance H to H	$-\alpha/2$	A	P	$0.8\,L\sin^2\theta$
90°	1.385	16.1	−5.7	−14.3	0
110°	1.606	10.2	−3.6	− 5.9	29
120°	1.697	8.2	−2.9	− 4.2	43

Column 2 of Table I gives the distance between two H atoms corresponding to the angle between the OH bonds given in Column 1. Column 3 gives the interchange repulsive energy; Column 4 the coulombic attraction; Column 5 the van der Waals attraction; Column 6 the positive potential due to distortion of the valence bond. The potential energies of Columns 3, 4 and 5 are zero when the H atoms are very far apart, whereas Column 6 depends only on the angle between the OH bonds. The van der Waals potential given in Column 5 is certainly much too large. All the energies are in kg. cal. The fact that the two OH bonds are polar will tend to increase the angle between the bonds. In spite of the approximateness of our calculations it is clear that steric effects are not to be neglected in H_2O. Also an angle differing greatly from 90° would be

[16] Slater, *Phys. Rev.*, **37**, 481 (1931); Pauling, THIS JOURNAL, **53**, 1367 (1931).

surprising because of the rapidity with which directed valence falls off with θ. Equation 5 is, however, only valid for small values of θ. The methods suggested for calculating the potential energy upon collision of complicated molecules suffice also to calculate steric hindrance in complicated cases. Collision potentials and steric hindrance are really two aspects of the same problem. Kinetic theory diameters are a convenient measure of the distance at which steric hindrance starts to be important.

With alcohols and ethers the angle between the oxygen bonds should be still further increased by the larger steric effects and this is what electric moments indicate.[17] A carbon to oxygen bond involves two directed eigenfunctions. If the axis of the carbon eigenfunction makes an angle, θ_1, with the line joining the atoms and the axis of the oxygen eigenfunction an angle, θ_2, with this same line, the bond varies with the angles approximately in the following fashion.

$$L \cos^2\theta_1 \cos^2\theta_2 + M(\sin^2\theta_1 \cos^2\theta_2 + \cos^2\theta_1 \sin^2\theta_2) + N \cos^2\theta_1 \cos^2\theta_2 \qquad (6)$$

The significance of L, M and N is made clear by substituting the value 0 and $\pi/2$ for θ_1 and θ_2 in various ways. In (6) many terms have been neglected, some of which are probably almost as large as the last term and it is only approximately true for small values of θ_1 and θ_2. Equation 6 is readily obtained by considering the interchange and coulombic integrals for a bond formed from two directed eigenfunctions. According to the views of Slater[16] and Pauling[16] each of the four valences of the carbon atom in the saturated hydrocarbons is approximately three-quarters a directed P valence, the remaining s valence is spherically symmetric. This introduces no difficulty in applying (6) to the directed part of the eigenfunction.

We shall now consider rotation about a single bond. Using the potential energy between two saturated H atoms given in Curve 2, Fig. 4, we can readily calculate the sum of the nine potentials between the hydrogen atoms on the two methyl groups in ethane. In Fig. 5 the sum of these nine potentials is plotted against angular displacement. Zero angle corresponds to the hydrogen atoms of one methyl group just eclipsing the hydrogen atoms of the other group as viewed along the C–C axis. Such an eclipse occurs three times in a revolution and accounts for the periodic nature of the potential. It is assumed that tetrahedral angles are preserved; that the C–C distance is 1.54 Å., and that the C–H distance in a methyl group is 1.13 Å. The distance between two H atoms on adjacent carbons is then given by the expression $d = (7.53 - 2.27 \cos\varphi)^{1/2}$, where φ measures the angular displacement of the two H atoms viewed along the C–C axis. If Curve II, Fig. 4, instead of I is used for estimating the potential between H atoms the ordinates in Fig. 5 are all approximately

[17] Smyth, *Chem. Rev.*, **6**, 549 (1929).

cut in two. The true potential curve will probably lie between these extremes. A detailed consideration of the physical properties of hydrocarbons will enable us to come to more precise conclusions and this is being done.

If one uses for the potential between saturated hydrogen atoms a repulsion corresponding to 35% of the Morse curve, which amounts to assuming that it is 10% coulombic and 90% interchange, and then adds to this a van der Waals potential, $101/r^6$, a somewhat larger potential is found than those given in Fig. 4. For some other atoms such assumptions lead to fairly good results. A systematic investigation of such potentials is being carried out.

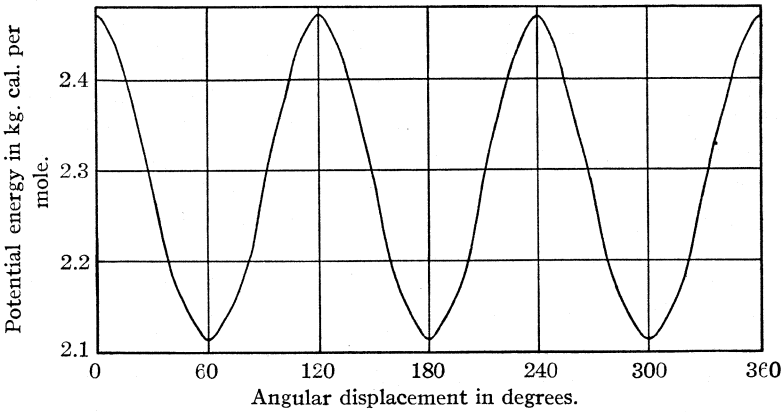


Fig. 5.—The dependence of the potential energy of the ethane molecule on rotation about the C–C bond.

As a final illustration of steric effects we will consider for hydrocarbons how the strength of a C—H bond is affected by successive substitution of CH_3 radicals for the other three hydrogen atoms in methane. Two hydrogen atoms in methane are at a distance from each other of 1.84 Ångströms. From Fig. 2 we find that half the theoretical interchange integral for this distance is -5.8 kg. cal. and the coulombic integral is -1.9 kg. cal. These values are probably each about 10% too low, since the corresponding integrals are about (but not more than) twenty-five per cent. too low when the atoms are 0.76 Ångströms apart and approach the correct values as the distance increases. The van der Waals attraction between hydrogen atoms cannot be satisfactorily estimated at such small distances with an expression of the type $101/r^6$ since this gives a fantastically large figure for the van der Waals attraction at 0.76 Å. for which the upper limit is the difference between the true heat of dissociation and that calculated by Sugiura. The van der Waals attraction is then considerably less than $101/1.84^6 = 2.62$ kg. cal. Ten per cent. of the sum of the interchange

plus coulombic integral, which is −1.4 kg. cal., cannot be far from correct. Using these figures we get for the total potential 5.8 − 1.9 − 1.4 = 2.5 kg. cal.

When a hydrogen atom in methane is replaced by a methyl radical, there is a corresponding change in the repulsion on any one of the remaining hydrogen atoms. The repulsion due to the hydrogens on the methyl group depends on the angular displacement of the methyl group about the C—C bond and is just one-third of the ordinate in Fig. 5. We must still estimate the repulsive potential due to the carbon atom in the methyl radical. For this purpose we shall assume a Morse potential curve with the following constants, $\omega = 2920$; $r_0 = 1.13$; $D = 92$. ω is the vibration frequency in wave numbers for the lowest level; r_0 is the normal distance in Ångströms between atoms and D is the heat of dissociation in kg. cal. If the C—C distance is taken as 1.54 Ångströms, then the distance from a carbon atom to a hydrogen atom on an adjacent carbon is 2.19 Å. The Morse curve gives 24.5 kg. cal. for the potential energy at this distance. If we assume this is eighty per cent. interchange binding and twenty per cent. coulombic plus van der Waals, the net repulsion is $[(0.80/2) - 0.20]\ 24.5 = 4.9$ kg. cal. This estimate is probably low since proper account has not been taken of the repulsion of three of the electrons on the carbon atom. As a final result then we find for the difference in the repulsive potential of a methyl group and a hydrogen atom on a single hydrogen atom the value $4.9 + (2 \times 1/3) - 2.5 = 3.1$, which is probably low rather than high. If the CH bond is assumed to have a strength of 120 kg. cal. everything else being the same, we obtain instead of 3.1 kg. cal., the value 5.6 kg. cal. We shall use the value 3.1 kg. cal. Thus, if we neglect changes in the bonds themselves, we should expect it to be hardest to remove a hydrogen from a carbon in methane, 3.1 kg. cal. easier to remove a hydrogen from ethane, 6.2 easier to remove a hydrogen atom from the central carbon in propane and 9.3 kg. cal. easier to remove a hydrogen from a carbon in which the other three bonds are methyl radicals.

The experiments of Bonhoeffer and Harteck[18] show that while hydrogen atoms will dehydrogenate other hydrocarbons, the reaction $H + CH_4 = H_2 + CH_3$ does not go. Since during a reaction of hydrogen with ethane the approaching H atom is much farther away from the methyl radical from which it does not remove a hydrogen than is the hydrogen removed, it is necessary to suppose that the principal effect of this methyl group is to weaken the bond of carbon to the attached hydrogen. The repulsion of the methyl group for the approaching hydrogen atom is negligible. The difference in rates observed is thus to be attributed to a stronger C–H bond in methane and not just to a higher activation energy. Ex-

[18] Bonhoeffer and Harteck, *Z. physik. Chem.*, [A] **139**, 64 (1929).

periments of von Hartel and Polanyi[19] show that sodium atoms more readily detach halogen atoms from ethyl than from methyl radicals. Here again we see the effect of the repulsive potential of methyl radicals. From this point of view the heat of combustion might be supposed greater for branched than for the corresponding straight chain hydrocarbons. However, the net heat effect is greatly complicated by attraction between groups slightly farther apart than those we have just found repel.[20] Isopentane evolves 5 kg. cal. more heat upon combustion than normal pentane but with some of the longer chains this effect is lessened and even reversed so that for comparison of heats of combustion a more detailed treatment is necessary.

I wish to thank Professor J. C. Slater for many helpful discussions.

Summary

The method of calculating the potentials between saturated molecules or groups of atoms is indicated and the potential energy curve for two colliding H_2 molecules is calculated and compared with experiment. The agreement is good. A potential energy curve for the collision of two saturated hydrogen atoms is given and used in constructing a potential for the rotation of the two methyl groups in ethane about the C—C axis. Viewed along the C—C axis the greatest potential occurs at eclipse of the far hydrogen atom by the near ones. The lowest potential corresponds to a position half way between two eclipses. The calculated change in potential is 0.36 kg. cal. The true value probably lies between 0.36 kg. cal. and half this amount. A similar calculation indicates that a hydrogen in ethane is at a potential at least 3.1 kg. cal. higher than a hydrogen in methane due to the greater repulsion of a methyl group than of a hydrogen atom. This fact explains the increase in reactivity of a hydrogen attached to carbon as the three neighboring hydrogens are replaced by methyl groups.

PRINCETON, NEW JERSEY

[19] Von Hartel and Polanyi, *Z. physik. Chem.*, [B] **11**, 97 (1930).

[20] "International Critical Tables."

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

THE ABSORPTION SPECTRA OF THE CHROMIUM AMMINE HYDRATES[1]

BY ROBERT IRVING COLMAR AND FREDERICK WILLIAM SCHWARTZ

RECEIVED APRIL 29, 1932 PUBLISHED AUGUST 5, 1932

Introduction

The aquo ammino chromic salts have been regarded by Werner[2] as indicating the close relationship between chromic ammine complexes and chromic salt hydrates. Schwarz[3] mentions the interesting colors exhibited by these compounds, noting that the color changes from yellow through red to violet as ammonia molecules are replaced by water molecules in hexammine chromic salts. Shibata, together with his co-workers,[4,5] and Luther and Nikolopulos[6] have published absorption spectra observations on several of the aquo ammino chromic salts though data for the complete series were not obtained. These investigators agreed that the substitution of a water molecule for an ammonia molecule in these ammines causes the visible absorption band (of the compound in solution) to shift in the direction of increasing wave length. Since their data were not precise enough to furnish an estimate of the magnitude of this shift, this research was undertaken to obtain the desired information.

Preparation of Compounds.—The compounds used in this investigation were prepared by standard methods described in the literature.[7]

Apparatus.—The absorption spectra measurements were obtained by the use of a Nutting Polarization Photometer in conjunction with a Constant Deviation Spectrometer. Both instruments were made by Wm. Gaertner and Co. For a description and method of operation of this

[1] This paper is based on part of a dissertation submitted by Robert Irving Colmar to the Faculty of the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Original manuscript received August 19, 1931.

[2] Werner, "Neure Anschauungen auf dem Gebiete der anorganische Chemie," 4th ed., Braunschweig, 1920.

[3] Schwarz, "The Chemistry of the Inorganic Complex Compounds," translated by Bass, John Wiley and Sons, Inc., New York, 1928, p. 38.

[4] Urbain and Shibata, *Compt. rend.*, **152**, 593 (1913); Shibata, *J. College Sci. Imp. Univ. Tokyo*, **37**, Art. 2 (1915).

[5] Shibata and Matsuno, *ibid.*, **41**, Art. 6, Mar. 20 (1920).

[6] Luther and Nikolopulos, *Z. physik. Chem.*, **82**, 361 (1913).

[7] Biltz, "Laboratory Methods of Inorganic Chemistry," by Heinrich and Wilhelm Biltz, translated by Hall and Blanchard, John Wiley and Sons, Inc., New York, 1928; Christensen, *J. prakt. Chem.*, **23**, 27 (1881); Pfeiffer, *Ber.*, **38**, 3592 (1905); Pfeiffer, *ibid.*, **40**, 3126 (1907); Werner, *ibid.*, **43**, 2290 (1910); Reisenfeld, *ibid.*, **37**, 3059 (1905); Nordenskjold, *Z. anorg. Chem.*, **1**, 126 (1892); Werner and Klein, *Ber.*, **35**, 277 (1902).

spectrophotometer, Wagner's book[8] may be consulted. The absorption cells consisted of various lengths (about 1.5 cm. diameter) of hollow cylinders with polished ends over which were slipped circular end-plates. Measurements were taken at room temperature, no form of temperature control being employed.

Molecular extinction coefficients were calculated from the formulas

$$\text{Molecular extinction coefficient} \equiv \text{M. E. C.} = -\log_{10} T/cd$$

where T was the transmission of a tube of solution, of concentration c molar, and a length of d centimeters. The value of T was obtained from the equation

$$T = \frac{\sin^2 x}{\sin^2 x^\circ}$$

where x was the value of the photometer disk angle necessary to produce a balance in the photometric field when the solution being measured was in the path of the light beam of the photometer and x° was the value of the photometer disk angle when no absorption cell was in place.

Precision of Measurements.—The average deviation of the mean of the M. E. C. was kept at about ± 1 unit throughout the visible spectrum by varying the number of observations. In the violet part of the spectrum, ten readings at each point were taken because of poor visibility and low illumination; otherwise, five readings were satisfactory. By using copper sulfate and potassium chromate solutions, which are accepted spectrophotometric standards, recognition of constant or residual errors was possible. From a consideration of the results obtained by comparing observations on these solutions with those furnished by the Bureau of Standards, the author believes that the precision measure of the M. E. C. is 5%, which is a good value for this type of measurement.

Results

By plotting the molecular extinction coefficient versus wave number (see Tables I and II; also Figs. 1 and 2) for each solution, a value of the wave number at which the extinction coefficient is a maximum, is obtained. These maximum values of the M. E. C. are plotted *versus* molecules of water replacing molecules of ammonia in the complex (see Fig. 3). On examining these curves, the following generalizations may be noted. (1) On substituting a water molecule for an ammonia molecule in either a chromium or cobalt complex (up to four substitutions) the wave number at which maximum absorption of light occurs is decreased 610 mm.$^{-1}$ (Fig. 3). (2) On substituting a water molecule for an ammonia molecule in a chromium complex, the value of the molecular extinction coefficient at the maximum of the absorption band is decreased successively 4.9 units (Fig. 4). (3) In the cobalt complexes an anomaly to the previous rule for

[8] Wagner, "Experimental Optics," John Wiley and Sons, Inc., New York, 1929, p. 158.

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS

Wave length in Ångström units	Wave number in mm.$^{-1}$	Hexammino-chromic chloride	Aquopentammino-chromic chloride	Diaquotetrammino-chromic chloride	Triaquotriammino-chromic chloride	Tetraquodiammino-chromic chloride	Hexaquo-chromic chloride
4500	22220	36.1	26.7	19.7	12.2	10.0	..
4550	21980	38.8	28.6	21.0	..	..	..
4600	21740	40.8	31.9	22.8	16.5	10.5	..
4650	21500	40.1	32.8	24.8	..	..	..
4700	21280	39.2	34.1	26.6	18.7	11.9	..
4750	21060	36.8	35.6	28.5	..	..	..
4800	20840	33.8	35.4	30.5	22.0	14.2	2.8
4850	20620	30.8	35.1	30.8	..	..	..
4900	20410	27.5	34.4	30.9	25.6	16.3	3.4
4950	20200	24.4	33.1	30.8	25.4	17.9	..
5000	20000	19.7	31.5	30.6	26.1	19.1	3.6
5050	19800	15.2	29.5	29.5	26.4	19.1	..
5100	19610	12.6	27.8	28.1	25.4	20.1	4.3
5150	19420	9.5	25.6	..	25.0	20.4	..
5200	19230	8.4	21.9	24.0	24.8	20.6	5.0
5250	19050		20.0	..	23.0	20.6	..
5300	18870		17.2	19.8	22.0	20.2	5.8
5350	18690		15.3	..	..	20.3	..
5400	18520		12.1	14.4	19.7	19.3	6.7
5450	18350		..	..	..	..	..
5500	18180		9.4	10.0	16.7	16.7	7.4
5550	18020		..	..	..	..	7.8
5600	17860		6.8	7.3	14.3	14.1	8.5
5650	17700		..		..	..	8.7
5700	17540		5.4		..	11.9	8.9
5750	17390		..		..	..	..
5800	17240		3.9		8.4	10.5	8.8
5850	17090		..		..	..	8.8
5900	16950		..		..	..	8.2
5950	16810		..		..	..	8.1
6000	16670		3.1		3.6	6.6	8.1
6050	16530				..	..	..
6100	16390				..	..	6.9
6150	16260				..	..	..
6200	16130				1.6	4.7	6.3
6250	16000						..
6300	15870						5.1
6350	15750						..
6400	15630						4.2
6600	15150						2.5

chromium complexes exists, for a decrease in the molecular extinction coefficient takes place on the substitution of the first molecule of water for ammonia but an *increase* is noted for the second entering water molecule. However, the shift in wave number (as in Rule 1) holds true (Fig. 4).

TABLE II

MOLECULAR EXTINCTION COEFFICIENTS

Wave length in Ångström units	Wave number in mm.$^{-1}$	Hexammino-cobaltic chloride	Aquopentammino-cobaltic chloride	Diaquotetrammino-cobaltic chloride	Chloropentammino-cobaltic chloride	Chloropentammino-chromic chloride
4500	22220	46.1	34.9	22.4	24.2	20.6
4550	21980	50.8	37.9	..	26.2	..
4600	21740	53.8	40.8	30.4	30.4	23.6
4650	21500	54.5	42.5	..	31.0	..
4700	21280	56.1	45.5	36.4	33.4	26.2
4750	21060	56.1	46.0	..	35.5	..
4800	20840	55.5	46.5	44.9	37.5	29.8
4850	20620	54.0	47.6	..	39.2	..
4900	20410	49.1	47.9	49.5	40.9	33.1
4950	20200	44.4	46.5	51.9	41.9	..
5000	20000	33.6	45.5	52.9	43.1	35.1
5050	19800	..	44.5	53.1	44.9	..
5100	19610	..	42.8	51.5	46.1	35.8
5150	19420	..	..	50.4	47.1	..
5200	19230	18.9	39.2	49.1	47.5	34.2
5250	19050	..	..	47.5	46.8	..
5300	18870	..	..	44.7	46.4	32.4
5350	18690	..	..	..	45.6	..
5400	18520	5.7	25.9	39.3	44.0	27.6
5450	18350	..	..	..	..	..
5500	18180	..	..	32.0	40.5	21.6
5600	17860	0.4	13.6	26.4	34.6	16.2
5700	17540		..	..	25.6	..
5800	17240		6.5	15.8	19.3	6.9
5900	16950		..	..	13.5	..
6000	16670		3.4	8.4	..	3.4
6100	16390				6.5	
6200	16130				..	
6300	15870				3.4	

(4) Referring to Fig. 3 it will be noted that the lines for chromium salts and cobalt salts are parallel. This would seem to indicate that the substitution of a cobalt atom for a chromium atom in a complex as in $[Cr(NH_3)_6]Cl_3$ to $[Co(NH_3)_6]Cl_3$ or in $[Cr(NH_3)_5(H_2O)]Cl_3$ to $[Co(NH_3)_5(H_2O)]Cl_3$ causes the wave number at which maximum absorption of light occurs to decrease 510 mm.$^{-1}$. In order to verify this assumption $[Cr(NH_3)_5(Cl)]Cl_2$ and $[Co(NH_3)_5(Cl)]Cl_2$ were prepared and their absorption spectra studied. The difference between their wave numbers at maximum absorption was 500 mm.$^{-1}$, a value not much different from that predicted by the above generalization. (5) The molecular extinction coefficients at maximum absorption for all cobalt compounds have higher values than those of the corresponding chromium compounds (Fig. 4). (6) The substitution of chlorine for an ammonia molecule decreases the wave number at maximum absorption 1970 mm.$^{-1}$.

Discussion

Shibata[4] believes that in solution the following equilibrium is rapidly established

$$[Co(NH_3)_5(H_2O)]Cl_3 \rightleftharpoons H_2O + [Co(NH_3)_5(Cl)]Cl_2$$

the chloro-pentammino salt being formed almost exclusively. As the reason for this belief he points out that, according to his measurements, the absorption spectra of the aquo and chloro compounds are nearly identical. The author finds that this is not the case, since aquo-pentammino-cobaltic chloride has a wave number at maximum absorption of 20,570, while chloro-pentammino-cobaltic chloride has a wave number of 19,200, a difference quite beyond the possibility of experimental error.

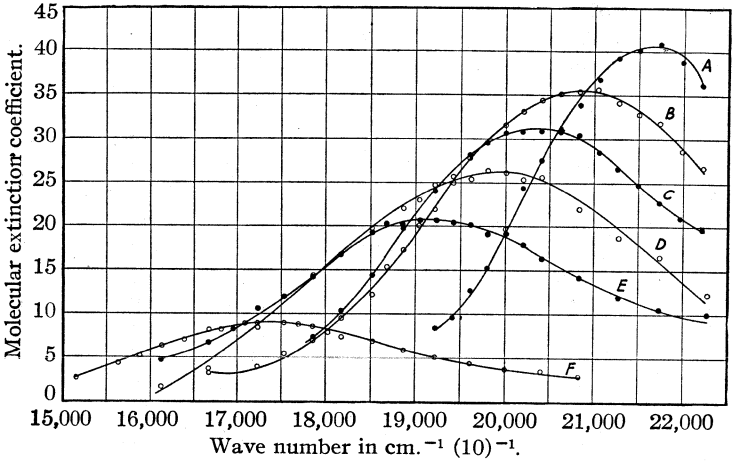


Fig. 1.—Absorption spectra of the chromium ammine hydrates: Curve A, hexammino-chromic chloride; B, aquo-pentammino-chromic chloride; C, diaquo-tetrammino-chromic chloride; D, triaquo-triammino-chromic chloride; E, tetraquo-diammino-chromic chloride; F, hexaquo-chromic chloride.

A similar difference is observed for the corresponding chromium salts. It is therefore believed that the absorption spectra furnish no evidence for such an hydrolysis (in freshly prepared solutions). However, the author has noticed that aquo-pentammino-*chromic* chloride changes into chloro-pentammino-chromic chloride in about a week, even if stored in the dark and over phosphorus pentoxide. It is therefore extremely likely that if a considerable interval elapsed between the preparation of the salts and their optical examination, erroneous results would be obtained.

Physical Theory.—From the fact that changes of the central atom produce variations in molecular extinction coefficients and wave numbers, it is evident that at least some (if not the greater part) of the color must be due to the central atom, or, strictly speaking, the central ion. This idea

furnishes a starting point in formulating a theory to explain the observed regularities.

For a basis the following principle, having wide application in spectroscopy, has been applied. If a molecule contains a number of energy absorbing units, capable of absorbing quanta denoted by $h\nu_1$, $h\nu_2$, $h\nu_3$, etc., then absorption of radiation energy, whose frequency is ν_1, ν_2, ν_3 and $\nu_1 + \nu_2 + \nu_3 + \ldots$, etc., may occur.

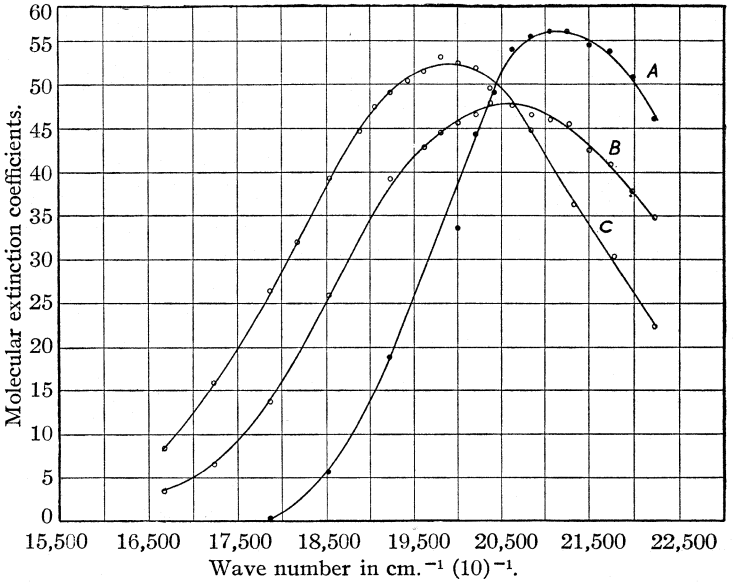


Fig. 2.—The absorption spectra of the cobaltic ammine hydrates: Curve A, hexammino-cobaltic chloride; B, aquo-pentammino-cobaltic chloride; C, diaquo-tetrammino-cobaltic chloride.

In any molecular group there may be a number of possibilities; these have been enumerated by Taylor:[9] (1) electronic transitions within individual atoms; (2) vibrations of the atoms within chemical groups; (3) rotation or quasi-rotation of the group as a whole.

Thus part of the light absorption capacity is attributed to the chromic ion or the cobaltic ion, because of an electronic transition within these ions. Another part is attributed to the internal vibrations of the atoms and ions making up the complex. Here, because of the great number of degrees of freedom possible in the system, many modes of vibration are possible, though it seems reasonable to expect that one or two modes will predominate.

The vibrational frequency (which is proportional to wave number) must be proportional to some function of the binding forces between the

[9] Taylor, *Trans. Faraday Soc.*, **25**, 860 (1929).

vibrating bodies and inversely proportional to some function of their masses.

The rotational frequencies are small, compared with electronic and vibrational frequencies, and are therefore neglected.

From the foregoing considerations, the absorption spectra of these complexes should show a strong absorption line (corresponding to $\nu_1 + \nu_2 + \nu_3 + \ldots$, etc.) surrounded by fine line structure (since there is a series of vibrational levels); instead a continuous band is observed. A number of reasons may be advanced for this, one of the most important being that given by Sidgwick,[10] who states "the broadening of the absorption lines of an ion in solution is due to the electric fields of neighboring atoms, which break up each line into components, whose separation depends on the strength of the field (Stark effect); as the ions present are thus affected in various degrees, the result is to spread the sharp lines into a band." The rotational frequencies must also contribute to the blurring of the lines as well as the collisions of the absorbing bodies in solution.

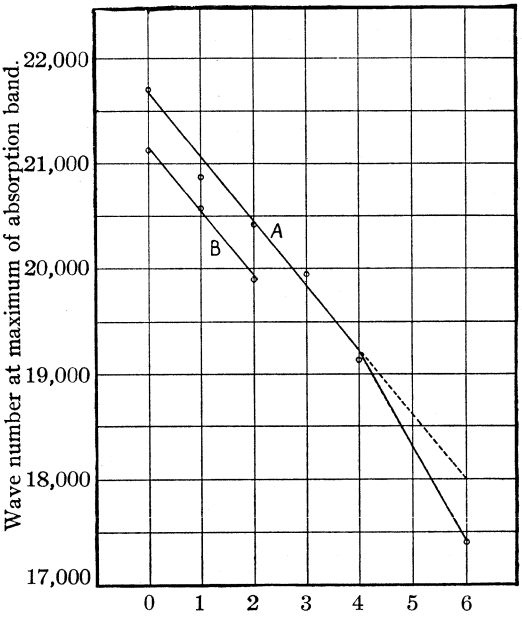


Fig. 3.—Curve A, chromic ammine hydrates; Curve B, cobaltic ammine hydrates.

Consider the compounds

(1) $[Cr(NH_3)_6]Cl_3$ (2) $[Co(NH_3)_6]Cl_3$ (3) $[Cr(NH_3)_5(H_2O)]Cl_3$

Since (1) and (3) have the same central ion, their electronic term must be the same and the shift in frequency, which is 1830 (10)[10] [the product of the velocity of light in centimeters and the difference between the wave numbers at maximum absorption of compounds (1) and (3)], is due to a change in the vibrational spectral terms. Since the masses of the ammonia and water molecules are approximately the same (17 and 18), it seems reasonable to attribute the change in vibrational frequency to a loosening of the binding forces which connect the ammonia and water groups to the central ion. This effect should be observed in an x-ray crystal analysis

[10] Sidgwick, "The Electronic Theory of Valency," The Clarendon Press, Oxford, England, 1927.

of these compounds. The hexammino salt should have the most compact structure, while the substitution of ammonia for water should loosen the crystal structure. The effect also should parallel the shifts in frequency: an anomaly should be observed for the hexaquo salt. Other evidence which supports this point of view comes from considerations of the chemical stability. The hexammine salts are the most stable, with the stability decreasing as water is substituted for ammonia, which is what would be expected from the binding forces becoming weaker.

The vibrational frequencies are affected by change of mass also, since the substitution of chlorine for ammonia causes a shift in frequency of 5910 units while a change of water for ammonia causes a shift in frequency of 1830 units. This also is to be expected on the basis of the theory.

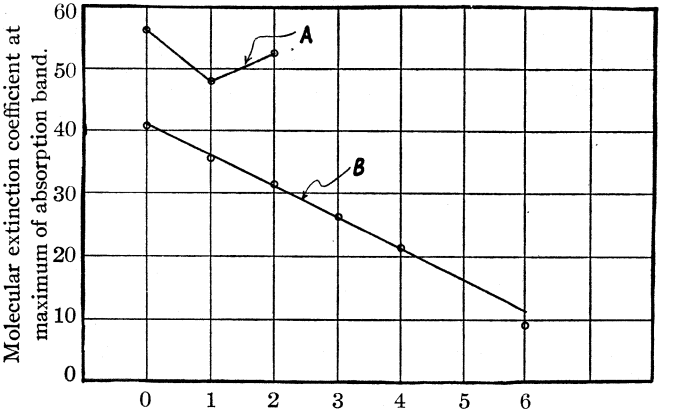


Fig. 4.—Curve A, cobaltic ammine hydrates; Curve B, chromium ammine hydrates.

Considering Compounds (1) and (2), the generalizations previously mentioned state that a decrease of 1530 units is to be expected on changing from Cr to Co. Since this difference of 1530 is constant for all compounds whose only difference is the central ion and the shift in frequency (1830) due to the substitution of water for ammonia remains the same for cobalt compounds, the only way to account for this is to assume that the vibrational terms for these compounds are the same or always differ by a constant amount. This attributes all change of color in these compounds to differences in the electronic terms. Since this electronic transition is a property of the central ion only, all complexes of cobalt and chromium, whose only difference in structure is a change of central ion, should show this same constant difference.

The explanation of the decrease in the value of the molecular extinction coefficients at the wave number of maximum absorption with the number of

substitutions of water for ammonia is related to the probability of electronic transitions within the group.

Acknowledgment.—This investigation was under the co-direction of Dr. Frederick William Schwartz, Professor of Inorganic Chemistry, and Dr. Robert Alexander Patterson, Professor of Physics, at the Rensselaer Polytechnic Institute. The author is deeply grateful to these men and others, who, by their interest and aid, contributed to the advancement of this research.

Summary

1. The visible absorption spectra of some chromammines and cobaltammines have been measured.

2. Certain empirical generalizations have been deduced from these measurements.

3. A theory has been put forth to account for the light absorption of complex compounds.

4. As a test of the theory, a prediction of the x-ray crystal analysis of a series of chromammines has been recorded.

TROY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE PRECISION WITH WHICH THE CONCENTRATIONS OF SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE MAY BE DETERMINED WITH THE IMMERSION REFRACTOMETER

BY E. ROGER WASHBURN AND ALLEN L. OLSEN

RECEIVED MAY 4, 1932 PUBLISHED AUGUST 5, 1932

The refractive index of solutions varies with the concentration. A curve may be prepared showing this variation and then if the refractive index of an unknown solution is determined, the concentration may be read from the curve, or calculated from the equation of the curve. In order to make an accurate determination, it is necessary that the solution contain no measurable amount of impurity and that the temperature at which the reading is taken be the same as that for which the curve and equation were determined. Since refractive index may be easily and accurately determined, it has been suggested[1] that the refractometer be used as a means of determining the concentrations of various standard solutions used in analytical chemistry.

The results of previous work on concentration–refractive index relation-

[1] H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **2**, 201 (1930); C. A. Clemens, *J. Ind. Eng. Chem.*, **13**, 813 (1921); B. Wagner, *Z. angew. Chem.*, **33**, 249 (1920).

ships are recorded in standard reference works.[2] A study of the original articles from which these tables have been compiled reveals the need for further work designed to determine the limits of precision within which the concentration of solutions may be measured by a study of the refractive index and precautions which must be taken in order to attain this accuracy. The usefulness of the method will be increased by the formulation of equations by which the normality may be calculated from refractive index.

Apparatus.—A Bausch and Lomb immersion refractometer, with a range of 1.32540 to 1.36639, was used in this investigation. A rectangular tank, provided by the makers of the instrument, was used to contain the cups of liquids during the time required to take the readings.

By siphoning water from an electrically heated, hand-controlled water-bath of thirty gallon capacity, we were able to maintain the temperature of the dipping tank to within $\pm 0.05°$ of the desired temperature during the time required to make the measurements. The temperatures in the bath and in the dipping tank were measured with calibrated thermometers graduated to 0.10°. The siphoned water in the refractometer tank was stirred with air, and the field was well illuminated with artificial light.

The pipets, burets and volumetric flasks used in preparing and standardizing the solutions were calibrated at 25.0°.

Solutions.—The water that was used in all of the experimental procedures was redistilled from an alkaline permanganate solution contained in a copper boiler fitted with a block tin condenser.

Hydrochloric Acid.—The hydrochloric acid solutions used in the major part of this study were prepared from freshly distilled samples of Grasselli C. P. quality acid. Some solutions were prepared by direct dilution of different samples of commercial C. P. acid. No significant differences were noted between the refractive indices of solutions of equal normality prepared from the two sources. The actual normality of each prepared solution was established by at least one of the following methods, gravimetric determination of silver chloride, the use of constant boiling hydrochloric acid prepared according to the method of Foulk and Hollingsworth[3] as a primary standard in making up the samples, or by quantitative dilution of a solution, the normality of which had been established by one of these procedures. The method used in each case is indicated in the table of results. All normalities were determined at 25.00°.

Sodium Hydroxide.—The sodium hydroxide solutions were prepared by the dilution of a saturated aqueous solution of Mallinckrodt reagent quality sodium hydroxide. Analysis[4] indicated that these solutions contained less than 0.5% sodium carbonate in terms of the sodium hydroxide content. The concentrations of the solutions of sodium hydroxide were determined by titration with hydrochloric acid which had been standardized by means of chloride analysis. Methyl orange was used as the indicator. Some of the test solutions were prepared by dilution of standard solutions and from the proportions used the concentrations were calculated. The solutions of sodium hydroxide

[2] Landolt-Börnstein, "Phys.-chem. Tab.," J. Springer, Berlin, Vol. II, 1923, pp. 988–990; "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, 1929, Vol. VII, pp. 65–76; B. Wagner, "Tabellen zum Eintauchrefraktometer," Sondershausen, 1907.

[3] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220–1228 (1923).

[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1928, 7th ed., Vol. II, p. 486.

were kept in bottles which had been coated with a rubber preparation designed to be resistant to alkali.[5] A few tests were run on solutions prepared by simply dissolving ordinary C. P. sodium hydroxide and U. S. P. X sodium hydroxide in water. The source of the different test solutions is indicated in the tables of results.

Measurement of Refractive Index.—Immersion refractometers are graduated in arbitrary scale divisions which may be converted into refractive indices by means of an equation or by conversion tables provided with the instrument. Since not all instruments have the same arbitrary scale, it is important to be sure that the conversion tables fit the instrument which is used. Our instrument was adjusted at each temperature to give the correct value for water. The uniformity of the scale and accuracy of the instrument were checked by measurement of the refractive indices of sodium chloride solutions. The results obtained, throughout the range of the instrument, checked accepted[6] values within ± 0.00003 at 25.0°.

In view of the fact that a 1° change in temperature is equivalent to about 0.3 of a scale division or 0.00012 in refractive index for water, it is evident that temperature variations must be small. The variation which we allowed ($\pm 0.05°$) is equivalent to about 0.015 scale division, which is less than the usual experimental error in reading the instrument. It was found necessary to wait several minutes after the refractometer was immersed in the solution for temperature equilibrium to be reached so that a sharp field and constant readings could be obtained.

That it is necessary to guard against evaporation from the liquid in the refractometer cups and that paraffined corks will effectively cut down evaporation are shown by the data in Table I. These readings were taken at 25.00° with an approximately 4 *N* solution of hydrochloric acid.

TABLE I

Open cups		Stoppered with paraffined corks	
Elapsed time, min.	Scale reading	Elapsed time, min.	Scale reading
0	99.56	0	99.56
24	99.58	20	99.58
69	99.57	62	99.55
108	99.63	103	99.55
221	100.03	254	99.57
994	101.62	917	99.68
1283	102.90	1263	99.68

The holes at each end of the rack in the dipping tank were not used as it was found that unequal illumination in these positions caused variable results.

The dipping prism of the refractometer is fastened in a mounting made

[5] Goodrich Thermoprene—Acid Seal Paint No. 1023, B. A. Soule, *Ind. Eng. Chem., Anal. Ed.*, **1**, 2 (1929).

[6] "International Critical Tables," The McGraw-Hill Book Co., Inc., New York Vol. VII, p. 73.

of an acid-resisting alloy. It was found that this dissolved slowly when in contact with concentrated solutions of hydrochloric acid and resulted in variable scale readings. The mounting was coated with a thin layer of paraffin which successfully prevented the corrosion and resulted in practically constant readings over a period of several hours.

Experimental Results

The refractive indices of a number of solutions of hydrochloric acid ranging in normality from 0 to 4, and of solutions of sodium hydroxide ranging in normality from 0 to 3, were determined at 20.00, 25.00 and 30.00°. The normalities of the solutions at 20.00 and 30.00° were calculated from the values measured at 25.00° making use of the densities and compositions listed in the "International Critical Tables."

From these results equations for each of the materials at each temperature were determined by substituting normalities and the corresponding refractive indices in the following general equation for a parabola:

$$N = A + B\,(\text{ref. index soln.} - \text{ref. index water}) + C\,(\text{ref. index soln.} - \text{ref. index water})^2$$

N represents the normality of the chosen solution. Since with pure water N is zero, A is also zero, so an equation for the curve may be formulated by solving two simultaneous equations for B and C. A fourth or D term to be multiplied by the cube of the difference in refractive indices was not used because it was found that for the range of concentrations studied the agreement between the results calculated without the D term and the actual normality was within the experimental error of the method. Slightly different values for these constants resulted from using different combinations of solutions. Several combinations were used and from the constants obtained those given in the equations in Tables II and III were chosen as seeming to represent closely the relation between normality and refractive index for the system studied.

Test solutions were then prepared and the normalities calculated from refractive indices were compared with those obtained by standard methods. Since the agreement in these examples is in no sense different from that found with the original solutions studied, the results are listed together in the same tables.

In the case of hydrochloric acid, the greatest difference between the calculated normalities and the actual normalities is ± 0.005. This amounts to an error of $\pm 5.0\%$ with a 0.1 N solution, but to only 0.5% for a 1.0 N solution or 0.13% for a 4 N solution. The average difference, however, is only ± 0.002, which would be a percentage error of ± 1.0, ± 0.1 and $\pm 0,05$ for 0.1 N, 1.0 N and 4.0 N, respectively.

The greatest difference between the calculated values and those obtained by analysis for sodium hydroxide is about ± 0.003 in normality

TABLE II

HYDROCHLORIC ACID AT 20.00°

$N = 119.1$ (ref. index HCl − ref. index H_2O) + 209 (ref. index HCl = ref. index $H_2O)^2$

Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
0.0000		1.33302		
.2430	Dil.	1.33507	0.2450	+0.0020
.4859	AgCl	1.33708	.4874	+ .0015
.8901	Dil.	1.34040	.8917	+ .0016
1.2562	AgCl	1.34336	1.2559	− .0003
1.5215	AgCl	1.34549	1.5196	− .0019
2.0262	Dil.	1.34950	2.0245	− .0017
2.5129	Dil.	1.35332	2.5116	− .0013
3.0401	AgCl	1.35738	3.0363	− .0038
3.4458	Dil.	1.36050	3.4468	+ .0010
4.0582	AgCl	1.36514	4.0612	+ .0030

At 25.00°

$N = 119.0$ (ref. index HCl − ref. index H_2O) + 253 (ref. index HCl − ref. index $H_2O)^2$

0.0000		1.33251		
.1216	Dil.	1.33351	0.1192	−0.0024
.2428	Dil.	1.33457	.2460	+ .0032
.3041	AgCl	1.33506	.3049	+ .0008
.4853	AgCl	1.33659	.4898	+ .0045
.8549	AgCl	1.33956	.8513	− .0036
.8890	Dil.	1.33988	.8911	+ .0021
1.2545	AgCl	1.34283	1.2558	+ .0013
1.5194	AgCl	1.34495	1.5182	− .0012
2.0233	Dil.	1.34893	2.0222	− .0011
2.5089	Dil.	1.35269	2.5051	− .0038
3.0351	AgCl	1.35675	3.0337	− .0014
3.4399	Dil.	1.35985	3.4431	+ .0032
4.0510	AgCl	1.36441	4.0541	+ .0031

At 30.00°

$N = 118.9$ (ref. index HCl − ref. index H_2O) + 267 (ref. index HCl − ref. index $H_2O)^2$

0.0000		1.33196		
.1214	Dil.	1.33299	0.1226	+0.0012
.1994	Const. boil.	1.33366	.2004	+ .0010
.2425	Dil.	1.33403	.2463	+ .0038
.2497	Const. boil.	1.33406	.2484	− .0013
.4440	Const. boil.	1.33566	.4411	− .0029
.6898	AgCl	1.33769	.6900	+ .0002
.8877	Dil.	1.33932	.8895	+ .0018
1.2525	AgCl	1.34227	1.2541	+ .0016
1.5170	AgCl	1.34435	1.5142	+ .0008
2.0200	Dil.	1.34833	2.0178	− .0022
2.6375	Dil.	1.35310	2.6328	− .0047
3.0298	AgCl	1.35610	3.0258	− .0040
3.4337	Dil.	1.35918	3.4341	+ .0004
3.9858	Const. boil.	1.36328	3.9884	+ .0026
4.0435	AgCl	1.36374	4.0482	+ .0047

TABLE III

SODIUM HYDROXIDE AT 20.00°

$N = 89.2$ (ref. index NaOH − ref. index H_2O) + 595 (ref. index NaOH − ref. index $H_2O)^2$

Source	Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
Water	0.000		1.33302		
Reagent	.197	Dil.	1.33517	0.195	− .002
Reagent	.328	Titr.	1.33660	.327	− .001
Reagent	.886	Titr.	1.34236	.884	− .002
Reagent	1.378	Dil.	1.34714	1.377	− .001
Reagent	1.805	Titr.	1.35110	1.805	.000
Reagent	2.462	Titr.	1.35685	2.463	+ .001
Reagent	2.791	Dil.	1.35962	2.793	+ .002
Reagent	3.288	Titr.	3.36364	3.289	+ .001

At 25.00°

$N = 90.7$ (ref. index NaOH − ref. index H_2O) + 585 (ref. index NaOH − ref. index $H_2O)^2$

Water	0.000		1.33251		
Reagent	.085	Titr.	1.33346	0.086	+0.001
Reagent	.197	Titr.	1.33467	.197	.000
Reagent	.265	Titr.	1.33543	.268	+ .003
Reagent	.327	Titr.	1.33605	.328	+ .001
Reagent	.478	Titr.	1.33763	.479	+ .001
Reagent	.538	Titr.	1.33826	.540	+ .002
Reagent	.625	Titr.	1.33912	.624	− .001
Reagent	.778	Titr.	1.34068	.778	.000
Reagent	.885	Titr.	1.34174	.886	+ .001
Reagent	1.376	Dil.	1.34644	1.375	− .001
Reagent	1.802	Titr.	1 35034	1.802	.000
Reagent	2.457	Titr.	1.35603	2.455	− .002
Reagent	2.785	Dil.	1.35879	2.785	.000
Reagent	3.280	Titr.	1.36279	3.280	.000
C. P.	0.116	Titr.	1.33379	0.117	+ .001
C. P.	.707	Titr.	1.33995	.706	− .001
C. P.	.756	Titr.	1.34043	.754	− .002
U. S. P. X	.143	Titr.	1.33407	.141	− .002
U. S. P. X	.323	Dil.	1.33602	.325	+ .002
U. S. P. X	.647	Titr.	1.33934	.647	.000

At 30.00°

$N = 92.3$ (ref. index NaOH − ref. index H_2O) + 550 (ref. index NaOH − ref. index $H_2O)^2$

Water	0.000		1.33196		
Reagent	.197	Dil.	1.33411	0.200	+0.003
Reagent	.326	Titr.	1.33551	.327	+ .001
Reagent	.884	Titr.	1.34108	.885	+ .001
Reagent	1.374	Dil.	1.34572	1.374	.000
Reagent	1.799	Titr.	1.34959	1.798	− .001
Reagent	2.452	Titr.	1.35530	2.453	+ .001
Reagent	2.779	Dil.	1.35803	2.780	+ .001
Reagent	3.273	Titr.	1.36204	3.273	.000

The percentage error would be ±3, ±0.3 and ±0.1 for concentrations of 0.1, 1 and 3 normal, respectively. The average difference is ±0.001. which, when applied to the three concentrations, would be a percentage error of ±1, ±0.1 and ±0.03.

The differences between the calculated and the observed normalities of hydrochloric acid and sodium hydroxide are found to fall within the limits of precision which one would calculate from the slopes of curves plotted from the values in Tables II and III and from the accuracy with which one may read the refractometer. One unit in the fifth decimal place in refractive index (0.00001) corresponds to about 0.0012 in normality for hydrochloric acid and to about 0.0009 in normality for sodium hydroxide. The makers of the instrument state that an ordinary worker is able to read scale divisions with a precision of ±0.2 and with a little practice to a ±0.1. One-tenth of a scale division is equivalent to 0.00004 in refractive index. Therefore

$$\begin{aligned} \pm 0.2 \text{ in scale readings} &= \pm 0.0096 \text{ in } N \text{ for HCl} \\ &\quad \pm 0.0072 \text{ in } N \text{ for NaOH} \\ \pm 0.1 \text{ in scale readings} &= \pm 0.0048 \text{ in } N \text{ for HCl} \\ &\quad \pm 0.0036 \text{ in } N \text{ for NaOH} \end{aligned}$$

Summary

The refractive indices for hydrochloric acid solutions up to 4 N and for sodium hydroxide solutions up to 3 N have been determined at 20.00, 25.00, 30.00°.

Equations relating normalities to refractive indices for these solutions have been formulated.

Several precautions which must be taken in order to obtain precision results with the immersion refractometer have been studied.

The limits of precision with which one may expect to determine the concentrations of these solutions by this method have been determined.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 318]

THE USE OF A SULFATE–HYDROSULFATE BUFFERED SOLUTION FOR THE PRECIPITATION OF ZINC SULFIDE

BY C. E. P. JEFFREYS AND ERNEST H. SWIFT

RECEIVED MAY 5, 1932 PUBLISHED AUGUST 5, 1932

It has been realized for over half a century that there are advantages in precipitating zinc sulfide from an acid solution rather than one which is neutral or alkaline; specifically, certain separations can be made by proper adjustment of the hydrogen-ion concentration and the precipitate usually separates in a form which is more readily handled. Because of these effects many early workers[1] recommended the use of various organic acids for acidifying the solution and thereby obtained, somewhat uncertainly, the effect of a buffered solution considerably prior to the development of the modern theory and use of such solutions.

Somewhat more recently the use of sulfuric acid solutions was studied by Weiss,[2] who recommended that the precipitation be made from a solution 0.01 *N* in sulfuric acid by means of a very rapid stream of hydrogen sulfide, but he apparently provided no means for controlling the increase in hydrogen ion concentration taking place during the precipitation; by Waring,[3] who once more recommended the use of formic acid; by Funk[4] who studied the effect of various organic acids on the precipitation and on the separation of zinc from various other elements; while Glixelli[5] made a comprehensive study of the effect of the nature of the solution on the forms and apparent solubility of the precipitate, also on the time factor which enters in establishing the precipitation equilibrium.

In the excellent work of Fales and Ware[6] the limits of the hydrogen-ion concentration between which quantitative precipitation could be effectively made were first precisely determined and means provided for controlling the acidity within these limits. They found that 0.01 *N* sulfuric acid solutions were near the limiting hydrogen-ion concentration above which precipitation is incomplete. Therefore they rejected sulfuric acid solutions in favor of formic acid–formate buffered solutions, and found that for such solutions the hydrogen-ion concentration most favorable for quantitative precipitation of zinc sulfide was 10^{-2} to 10^{-3}. They seem not to have

[1] (a) Deeffs, *Chem. News*, **41**, 279 (1880); (b) Bragard, Dissertation, Berlin, 1887; *Z. anal. Chem.*, **27**, 209 (1888); (c) Beilstein, *Ber.*, **11**, 1715 (1885); (d) Mühlhäuser, *Z. angew. Chem.*, **15**, 731 (1902); (e) Berg, *Z. anal. Chem.*, **25**, 512 (1886); (f) Dohler, *Chem.-Ztg.*, **23**, 399 (1899); (g) Neumann, *Z. anal. Chem.*, **28**, 57 (1889).

[2] G. Weiss, Dissertation, München, 1906.

[3] Waring, THIS JOURNAL, **26**, 26 (1904).

[4] Funk, *Z. anal. Chem.*, **46**, 93 (1907).

[5] Glixelli, *Z. anorg. Chem.*, **55**, 306 (1907).

[6] Fales and Ware, THIS JOURNAL, **41**, 487 (1919).

investigated the possibility of using sulfate and hydrosulfate as a buffer for controlling the acidity during the precipitation.

Lundell, Hoffman and Bright[7] have recently recommended the precipitation of zinc sulfide from a 0.01 *N* sulfuric acid solution and state that the best precipitation is obtained from a sulfuric acid–sulfate solution. They do not present any discussion or experimental data in support of this recommendation.

This paper presents the results of a study of the use of sulfate–hydrosulfate mixtures as buffer solutions, of the precipitation of zinc as zinc sulfide from such solutions, and of the separation of zinc under such conditions from nickel, cobalt, iron, manganese, chromium and aluminum.

There are certain advantages in using sulfate–hydrosulfate buffered solutions for this particular precipitation. The second ionization constant of sulfuric acid having been determined[8] as 1.15×10^{-2}, and the optimum hydrogen-ion concentration for the precipitation of zinc sulfide from sulfate solutions having been found to be about 10^{-2}, it would seem that the required ratio of sulfate to hydrosulfate should be about one, the most favorable ratio for effective buffer action. As compared with this, Fales and Ware had to use an acid-to-salt ratio of 84:1, with the formic acid concentration 4.7 formal, in order to obtain an initial P_H of 1.86, a value at which, in our experiments, quantitative precipitation was obtained. This P_H was experimentally obtained in the sulfate–hydrosulfate solution by using an acid-to-salt ratio of 20.7:66, with the total concentration of sulfate and hydrosulfate 0.347 formal. In addition, Fales and Ware recommended the use of considerable ammonium citrate and 6.25 g. of ammonium sulfate in 200 ml. of solution. It is stated that: "ammonium citrate is used for the purpose of forming complexes with interfering metals," thus assisting in holding in solution such elements as iron and manganese. We find that from a sulfate–hydrosulfate solution of the proper P_H, such an agent is not needed. The ammonium sulfate was added as a "salting-out agent." In our experiments the need of adding an additional salting-out agent was not apparent, as quantitative precipitation was obtained, and as the form of the precipitate left nothing to be desired as to ease of filtration and washing. It is believed that under the conditions of our experiments, the hydrogen-ion concentration is the predominant factor governing the form as well as the solubility of the precipitate. It should also be mentioned that when using this precipitation of zinc as a means of effecting a qualitative separation it is a decided advantage not to have to add organic matter to the solution, for, especially in a group analysis, such material as citrates may cause difficulties in subsequent operations.

[7] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, 1931, p. 388.

[8] Sherrill and Noyes, THIS JOURNAL, **48**, 1873 (1926).

This study was originally undertaken in order to devise a suitable method for the qualitative separation of zinc from nickel and cobalt which would be more quantitative than those commonly employed in qualitative systems, such as, for example, the treatment of the mixed sulfides with dilute hydrochloric acid or the use of sodium hydroxide and peroxide. We wish to express our obligation to Mr. W. H. Pickering and to Mr. D. F. Bender for a large number of preliminary experiments in which the limiting conditions were determined and in which the effect of such modifications as carrying out the precipitation at elevated temperatures under considerable pressure of hydrogen sulfide was studied.

Materials

Preparation and Standardization of a Zinc Sulfate Solution.—A C. P. grade of zinc sulfate was recrystallized once from distilled water and once from conductivity water. The solution, saturated at 70°, was cooled in an ice-bath and the crystals collected by suction filtration. A stock solution containing approximately 40 mg. per ml. was made, and a working solution containing 10 mg. per ml. was prepared from it by dilution. This latter solution was standardized by precipitating the zinc as sulfide from sulfate–hydrosulfate solutions at such a P_H that the precipitation was quantitative, *i. e.*, initial P_H's of 2.18 and 1.86. The zinc sulfide was then converted to sulfate and weighed as such. The values thus obtained were 257.0 mg. per 25 ml. and 257.3 mg. per 25 ml. Some difficulty was experienced in igniting the zinc sulfate samples to constant weight. Fales and Ware, after igniting the paper and precipitate, added concentrated sulfuric acid and heated to constant weight in an air-bath. With their particular arrangement they mention no difficulty. Scott[9] directs that the zinc sulfate be ignited to dull red heat. It was found difficult to drive off all the sulfuric acid on an air-bath, and very difficult to ignite with a Bunsen burner without decomposing some of the sulfate. However, constant weight was easily obtained by fuming off the excess acid on an air-bath and heating the precipitate to 500 ± 20° for one hour (an electric furnace with a temperature indicator and control was used). Lundell, Hoffman and Bright[7] recommend igniting to zinc oxide at 900°, and indicate that in this case also the temperature of ignition must be fairly closely controlled. Our experiments confirmed this and indicate that either method is capable of consistent results with careful control of the temperature of ignition.

The Gases Used.—Hydrogen gas for the hydrogen electrode was taken from a cylinder. Using standard buffer solutions it was found that with this hydrogen constant and reproducible e. m. f. values were obtained which agreed with the accepted values for these solutions. Hydrogen sulfide, also from a cylinder, was used after passing it through a bottle of distilled water. Carbon dioxide was obtained from a cylinder.

Buffer Solutions.—The buffer solutions were made by weighing out the proper quantity of C. P. sodium sulfate decahydrate, and adding the required amount of either standard sulfuric acid or a weighed quantity of C. P. sodium hydrosulfate.

Sulfates of Other Metals.—The best available C. P. grade sulfates of cobalt, iron, nickel and manganese were used without further purification. Qualitative tests showed that the cobalt contained no nickel, and the nickel no cobalt. The source of the chromium and aluminum were C. P. grades of potassium aluminum sulfate and potassium chromium sulfate.

[9] Wilfred W. Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., 1927, p. 599.

The Experiments

P_H Measurements on the Buffer Solutions.—The buffer solution was made up in a 500-ml. Erlenmeyer flask, and 25 ml. of zinc sulfate solution containing 257 mg. of zinc was added with a pipet. The total volume in all experiments was 250 ml. The P_H of the solution was measured by means of a Hildebrand type bubbling electrode, and a saturated calomel half-cell. The electrodes and assembly for the hydrogen-ion concentration measurements were checked against a standard acetate solution, and also against a $M/20$ potassium acid phthalate solution. A sample of Bureau of Standards potassium acid phthalate was used for checking an electrode, then with the same electrode a solution prepared from a C. P. brand of potassium acid phthalate was measured. The e. m. f.'s agreed to within one millivolt. This latter solution was then used for checking the electrode from time to time during the course of the work.

Precipitation of the Zinc Sulfide.—The method of precipitation closely followed that given by Fales and Ware.[10] The solution from which the zinc was to be precipitated was heated to 60°, hydrogen sulfide bubbled through rapidly and the heating continued until the temperature reached 90–95°. As the solution cooled, hydrogen sulfide was also bubbled through it until the precipitate began to settle rapidly, and finally the solution was saturated when cold. Twenty-five to forty minutes were usually required before rapid settling was obtained. The precipitation was found to be quantitative in forty minutes when carried out in this way in solutions of the proper acidity.

The mixtures were allowed to stand until the supernatant liquid was entirely clear. Some solutions were filtered after standing for three hours, and others were allowed to stand overnight; no difference was detected as to ease of filtering or completeness of precipitation. The precipitate was of a dense, granular form, which filtered rapidly and did not cling tightly to the glass of the flask as is the case with zinc sulfide precipitated from less acid or alkaline solutions.

P_H Measurements on the Filtrate.—The filtration was made through a dry paper, the filtrate freed of hydrogen sulfide by bubbling carbon dioxide through it, and the P_H measured after removing the carbon dioxide by passing hydrogen through. A blank was run on a solution made up as was the solution in Expt. 3 of Table I. Instead of precipitating the zinc in this case, an amount of sulfuric acid was added corresponding to the acid liberated on precipitating 257 mg. of zinc. The P_H change was from 1.86 to 1.68, which corresponds closely with the change observed in the experiments shown in the tables.

The Solubility of Zinc Sulfide in Sulfate–Hydrosulfate Solutions.—In Table I are given the results of a group of experiments in which the

[10] Ref. 6, p. 493.

solubility of zinc sulfide with various ratios of hydrosulfate to sulfate and various P_H values was studied. Column 2 gives the ratios of $NaHSO_4/Na_2SO_4$ initially in the solution, columns 3 and 4 the initial and final P_H values, respectively, and column 5 the milligrams of zinc remaining in solution after the precipitation with hydrogen sulfide. The values in the last column were obtained in the following way. After making the final P_H measurement, ammonia was slowly added to the filtrate until it remained just acid to litmus, and again hydrogen sulfide was passed in to precipitate any zinc which had remained in the filtrate. The size of the precipitate thus obtained was compared with that obtained on precipitating known quantities of zinc under the same conditions. Fales and Ware[6] estimated the unprecipitated zinc by weighing the precipitate obtained and calculating the difference from the amount taken. The method here used is a more direct way of estimating the small amounts of zinc remaining in solution, and is sufficiently accurate for estimating the quantities involved. Confirmatory experiments showed that under these conditions 0.1 mg. of zinc would give a detectable opalescence on treatment with hydrogen sulfide. A blank was run to prove that no free sulfur would be obtained under the same conditions. This possibility was minimized by the fact that the solution had been freed from oxygen by being saturated with carbon dioxide, and contact with air thereafter prevented so far as possible.

TABLE I

THE SOLUBILITY OF ZINC SULFIDE IN SULFATE–HYDROSULFATE SOLUTIONS OF VARIOUS HYDROGEN-ION CONCENTRATIONS

Volume, 250 ml. Zinc taken, 257 mg.

Expt.	Initial ratio $NaHSO_4/Na_2SO_4$ in millimoles	P_H initial	P_H final	Zinc found in the filtrate, mg.
1	8.3/66	2.18	1.83	0.0
2	12.4/66	2.08	1.78	Trace
3	20.7/66	1.86	1.66	0.20
4	22.8/66	1.78	1.62	Trace[a]
5	24.9/66	1.77	1.62	0.1–0.2
6	27.0/66	1.72	1.57	0.3–0.5
7	27.0/66	1.72	1.56	0.3–0.5
8	27.0/66	1.72	1.58	0.3–0.5[a]
9	27.0/66	1.72	1.58	0.3–0.5[b]
10	31.0/66	1.67	1.47	0.3–0.5[b]
11	37.3/66	1.57	1.46	0.5
12	45.0/66	1.49	1.39	0.8–1.0
13	58.0/66	1.38	1.29	1.5
14	70.5/66	1.31	1.22	4.0
15	87.2/66	1.19	1.14	6.0

[a] Filtered after standing for three hours. [b] Filtered after standing overnight.

From the above experiments it may be concluded that from these solutions precipitation will be complete to less than 0.25 mg. at a P_H of 1.6 or

at a hydrogen-ion concentration as high as 2.5×10^{-2}. Less than 1 mg. remains in solution at a P_H of 1.54 or hydrogen-ion concentration of 2.9×10^{-2}. It would seem that the conditions of Expt. 4, where the ratio of $NaHSO_4/Na_2SO_4$ is about one-third and the initial P_H 1.78, are best adapted for securing the desired completeness of precipitation of zinc and for holding other elements in solution. At the same initial P_H the solubility of the zinc sulfide in these solutions is about the same or even a little less than in the formic acid–formate solutions of Fales and Ware, in spite of the fact that in our experiments 257 mg. of zinc is precipitated as compared to about 162 in theirs, with consequently more acid liberated due to the precipitation. If desired the buffer action could be made considerably more effective and the change in hydrogen-ion concentration during precipitation made much smaller by increasing the concentrations of sulfate and hydrosulfate in the solution. This effect is shown in the last three experiments of Table I, where with a higher concentration of hydrosulfate the change during precipitation is less than 0.1 of a P_H unit. We have considered it desirable, in order to minimize difficulty in washing the precipitate and to avoid the use of excessive quantities of buffer material, to keep the buffer concentrations at the lowest values which would adequately control the acidity. It should be pointed out that due to the high concentration of electrolyte in these solutions, the evaluation of the activities of the various ions is subject to considerable uncertainty, while a simple calculation of the hydrogen-ion concentration from the formal salt/acid ratios may lead to results considerably divergent from the experimental values. Because of this a series of experiments was made to show the effect of dilution on the P_H of such a solution. The results are given in Table II.

TABLE II

THE EFFECT OF DILUTION ON THE P_H OF SULFATE-HYDROSULFATE SOLUTIONS

Experiment	1	2	3	4	5
$NaHSO_4$ [moles/liter]	0.1	0.05	0.025	0.01	0.0025
Na_2SO_4 [moles/liter]	0.5	0.25	0.125	0.05	0.0125
P_H	1.78	1.48	2.17	2.43	2.82

The decrease in acidity in the more dilute solutions is due to the fact that the fraction of the hydrosulfate ionized into hydrogen and sulfate ions becomes large at these concentrations; the increase in the more concentrated solutions would be predicted because of the effect of the high salt concentrations on the activities of the various ions. It is thus seen that if, in order to control more closely the acidity, a higher concentration of the buffer is used, the initial ratio of hydrosulfate to sulfate should be adjusted accordingly, thus with the sodium sulfate concentration 0.25 formal, a $NaHSO_4/Na_2SO_4$ ratio of one-third is required to produce an initial P_H of 1.78; with the sodium sulfate concentration 0.5 formal this ratio has to

be reduced to one-fifth. The effect of the use of ammonium sulfate was tested in two additional experiments which were duplicates of Expt. 4 except that ammonium sulfate and sulfuric acid were used to adjust the initial hydrosulfate-to-sulfate ratio to the value 22.8/66. No difference could be detected in either the rate or completeness of the precipitation or the nature of the precipitate. This indicates that neither the hydrogen-ion activity nor the salt effect had been greatly changed, and that where desirable ammonium sulfate can be substituted for the sodium salt.

Effect of Chloride Ion on the Precipitation of Zinc Sulfide.—In the following table is gathered a group of experiments in which the solution contained in addition to the buffer mixture 132 milli-equivalents of potassium chloride.

TABLE III

THE EFFECT OF CHLORIDE ION ON THE SOLUBILITY OF ZINC SULFIDE

Potassium chloride added, 132 milli-equivalents. Zinc taken, 257 mg. Volume, 250 ml.

Expt.	Initial ratio $NaHSO_4/Na_2SO_4$ in millimoles	Initial P_H	Final P_H	Zinc found in the filtrate, mg.
16	20.7/66	1.73	1.51	1.5
17	27.0/66	1.62	1.46	2.0
18	37.3/66	1.43	1.37	2.0

The presence of a high concentration of chloride ion lengthens the induction period in the beginning of precipitation, apparently slows down the precipitation and, with the same P_H, increases the solubility of zinc sulfide by three or four times. This is shown by comparing the results in Table III with those obtained at corresponding P_H values in Table II. It should be noted also that the presence of the potassium chloride increases the acidity in solutions where the initial hydrosulfate and sulfate ratios and concentrations are the same; for example, compare Expt. 16, Table III, with Expt. 3, Table I.

The Separation of Zinc from Cobalt, Nickel, Iron, Manganese, Chromium and Aluminum.—The following table gives a group of experiments showing the efficiency of the separation of zinc from the common metals most likely to be found with it after an ammonium sulfide precipitation.

The cobalt brought down with the zinc precipitate in Expt. 19 was determined by the method of Engle and Gustavson,[11] after dissolving the precipitate with hydrochloric acid. In Expt. 20 the precipitate was dissolved in acid, the solution made just alkaline, and sodium peroxide added. The black cobaltic oxide was easily detectable. The nickel in the zinc sulfide precipitate was estimated by dissolving the precipitate, making the solution barely basic with ammonia, and adding dimethylglyoxime. The quantity of glyoxime precipitate was estimated by comparison with precipitates obtained with known quantities of nickel under the same condi-

[11] Engle and Gustavson, *J. Ind. Eng. Chem.*, **8**, 90 (1916).

TABLE IV

SEPARATION OF ZINC FROM OTHER METALS

Volume, 250 ml. Initial ratio $NaHSO_4/Na_2SO_4$ in millimoles, 20.7/66 (except Expt. 20). 257 mg. zinc and 250 mg. of other metal taken unless otherwise stated under remarks.

Expt.	Other metal	P_H initial	P_H final	Other metal in ZnS ppt., mg.	Remarks
19	Co	1.82	1.64	7	200 mg. Co
20	Co	1.35		Trace	200 mg. Co. Initial ratio $NaHSO_4/Na_2SO_4$ = 58/66
21	Co	1.82		Large quant.	100 Zn; 400 Co
22	Co	1.82		No ppt.	No Zn, 500 Co; sol. stood 3 days
23	Ni	1.82	1.66	0.3–0.4	
24	Ni			0.3–0.4	
25	Mn	1.81	1.65	0.1	
26	Mn			0.1	
27	Fe	1.82	1.65	0.5–0.6	
28	Fe			0.5–0.6	
29	Al			<0.25	
30	Cr			0	

tions. Manganese was estimated by adding sodium bismuthate to the nitric acid solution obtained by dissolving the precipitate, then making comparisons of the color developed with that obtained on oxidizing known amounts of manganese. Iron was determined by comparison with standards to which potassium thiocyanate had been added. The precipitates from Expts. 29 and 30 were dissolved in hot 6 *N* hydrochloric acid and the solutions then made just basic to methyl red with ammonia. No chromium hydroxide and a bare trace of aluminum hydroxide formed. This precipitate was compared with standards.

From the results shown in Table IV it is seen that the separations are satisfactory in all cases except with cobalt. Even in a solution whose initial P_H was 1.35, too high in acid for complete precipitation of zinc, cobalt is still co-precipitated. In Expt. 21 where 100 mg. of zinc is precipitated from a solution containing 400 mg. of cobalt, the zinc sulfide precipitate came down quite white for several minutes, then the precipitate darkened rapidly and finally was almost black in color.

This effect appears to be similar to the induced precipitation of zinc sulfide by copper sulfide in more concentrated acid solutions which has been studied recently by Kolthoff and Pearson.[12] This effect they designate "post-precipitation" and attribute it to an induced precipitation of the zinc sulfide from a supersaturated solution, the induction being caused by adsorption of hydrogen sulfide on the copper sulfide. Under the conditions of certain of their experiments this adsorption became effective in promoting the precipitation of the zinc sulfide only after quantitative precipitation of the copper sulfide had taken place. That the effect obtained

[12] Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

here is a case of either promoted or of co-precipitation is shown by Expt. 22. This solution, which was identical with that in Expt. 21, but contained 500 mg. of cobalt alone, was saturated with hydrogen sulfide in the usual way, except that the gas was bubbled through for more than an hour; then the flask was closed and allowed to stand for three days. No cobalt sulfide precipitated. Fales and Ware report that cobalt cannot be separated from zinc by hydrogen sulfide precipitation from formic acid–formate solutions. It is of interest to mention that when a few milligrams of cobalt are precipitated with zinc sulfide, as in experiment No. 19, the resulting precipitate is colored green. This phenomenon was noted in a large number of experiments.

Method Recommended for the Precipitation of Zinc Sulfide, and the Separation of Zinc from Nickel, Iron, Manganese, Chromium and Aluminum.—As a result of the above experiments the following procedure is recommended. To a chloride-free solution of the zinc as sulfate in a 500-ml. flask add sodium (or ammonium) sulfate and hydrosulfate (or sulfuric acid) until the hydrosulfate to sulfate ratio is approximately 1:3 with the total concentration of sulfate and hydrosulfate about 0.35 formal.[13] Dilute the solution to 250 ml., heat it to 60°, rapidly bubble hydrogen sulfide through it and continue heating until the solution reaches 90–95°. Continue the passage of hydrogen sulfide until the precipitate settles rapidly, cool the mixture, again saturate it with the gas, close the flask and allow it to stand until the supernatant liquid is clear. Filter the mixture through a quantitative paper filter and wash the precipitate with 0.01 *N* sulfuric acid saturated with hydrogen sulfide.

If a gravimetric determination is desired, the precipitate is dried and ignited at as low a temperature as possible, care being taken to avoid the formation of zinc oxide. The cold residue is moistened with concentrated sulfuric acid and the excess fumed off on an air-bath. If carbonaceous material remains it is burned off by carefully heating with a Bunsen flame. Again the residue is moistened with sulfuric acid, the excess fumed off on the air-bath, and the precipitate either heated to 500° and weighed as zinc sulfate, or heated to 900° and weighed as zinc oxide. It is recommended that the temperature of the ignition be controlled to ±20°.

[13] Solutions containing zinc sulfate and an unknown excess of sulfuric acid can be neutralized with standard sodium hydroxide, preferably using methyl red as indicator, then the proper amounts of sulfate and hydrosulfate added. With aluminum present methyl orange should be used as the indicator; before neutralizing the solution ferric salts should be reduced with sulfur dioxide and the excess expelled; in neutralizing highly colored solutions containing large amounts of cobalt or nickel the formation of the first permanent precipitate can be used satisfactorily. With large amounts of the elements, especially of aluminum, account should be taken of the approximate amount of sulfate associated with them. Volatile acids can be removed by gentle fuming with sulfuric acid.

Summary

The precipitation of zinc sulfide from sulfate–hydrosulfate solutions has been studied. The precipitation was found to be complete to less than 0.25 mg. out of 257 mg. at a hydrogen-ion concentration as high as 2.5×10^{-2}. Nickel, iron, manganese, chromium and aluminum may be separated quantitatively from zinc by this sulfide precipitation, but cobalt cannot be so separated. High chloride-ion concentration increases the solubility of the zinc sulfide. A procedure is outlined for the quantitative precipitation of zinc and its separation from the other metals. Methods of igniting the precipitate have been studied. The temperature should be closely controlled at 500° when igniting the zinc sulfate, and at 900° when igniting the sulfate to oxide.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE DIRECT PREPARATION OF HYDROGEN PEROXIDE IN A HIGH CONCENTRATION

BY JAMES H. WALTON AND GEORGE W. FILSON

RECEIVED MAY 6, 1932 PUBLISHED AUGUST 5, 1932

The fact that hydrazobenzene is readily autoxidized with the formation of hydrogen peroxide has been pointed out by Manchot and Herzog.[1] In an investigation carried out in this Laboratory it was found that in an alcoholic solution the reaction is practically quantitative according to the equation

$$C_6H_5NHNHC_6H_5 + O_2 = C_6H_5N{=}NC_6H_5 + H_2O_2$$

As would be expected a small amount of the alcohol is oxidized by the hydrogen peroxide. The reaction takes place very readily in either ethanol or propanol. By dissolving hydrazobenzene in alcohol and bubbling oxygen through the solution it is possible to follow the speed of reaction by measuring colorimetrically the increasing color of the solution caused by the formation of the azobenzene. The reaction apparently takes place between the dissolved oxygen and the hydrazobenzene, so that in studying the speed of the reaction it is necessary to bubble the oxygen through the solution fast enough to keep the solution saturated. The reaction is bimolecular as evidenced by the following data taken from a series of experiments.

Temp., 30°; 1% solution of hydrazobenzene in 95% C_2H_5OH

t, min.	$a - x$	x	$k \times 10^4$
0	33.1		
16	20.6	12.5	11.4

[1] Manchot and Herzog, *Ann.*, **316**, 331 (1901).

t, min.	$a - x$	x	$k \times 10^4$
26	17.0	16.1	11.0
36	14.5	18.6	10.8
46	12.2	20.9	11.3
62	10.8	22.3	10.1
105	6.6	26.5	11.5
		Av.	11.0

In the experiment recorded the oxygen was released at the bottom of a Nessler tube containing 50 cc. of solution, through a delivery tube with an opening of about 1 mm. In another experiment with a delivery tube opening of 2 mm. bore the value of $k \times 10^4$ was 10.6, when the oxygen was passed through a group of five small jets of 0.5 mm. each, the constant was 9.7. Oxygen was bubbled through these delivery tubes without regard to the absolute rate, the object being to keep a rapid stream of bubbles flowing from each jet. The fact that the constants agree shows that the reaction is taking place in solution and not at the gas–liquid interface. The reaction when carried out in a tube covered with tin foil gave a constant of 10.2 showing that diffused light has no appreciable effect. In absolute ethyl alcohol the constant had a value of 3.4×10^{-4} while in isopropyl alcohol the speed of oxidation was somewhat slower, 4.2×10^{-5}.

Autoxidation in Benzene Solution.—In an effort to isolate an intermediate product of the peroxide type, the hydrazobenzene was oxidized in benzene solution. The concentration of the oxygen in the solution was increased by placing it in a bomb, lowering the temperature to 0° and increasing the oxygen pressure to about 370 pounds per square inch. No intermediate compound could be detected. However, drops of liquid separated from the benzene solution, which when analyzed were found to be hydrogen peroxide of a purity of about 94%. The total yield of hydrogen peroxide was determined and it was found that from a given weight of hydrazobenzene it was possible to obtain about 97% of the theoretical yield of hydrogen peroxide.

This quantitative yield of highly concentrated hydrogen peroxide from hydrazobenzene suggests the possibility of production of the peroxide on a large scale. Its attractive feature, of course, lies in the fact that the azobenzene formed in the reaction can be changed to hydrazobenzene and thus used continuously. The problem is the subject of further investigation.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. IX. THE OXYGEN AND SULFUR VALENCE ANGLES

BY C. P. SMYTH AND W. S. WALLS

RECEIVED MAY 7, 1932 PUBLISHED AUGUST 5, 1932

A previous paper[1] has described the determination of the carbon valence angle in benzyl derivatives as the angle between two component dipole moments, the resultant of which is the moment of the molecule as a whole. Since the dipoles are so far removed from one another by interposition of the benzene ring that they apparently do not affect one another's moments appreciably, a very satisfactory result was obtained. The present paper attempts to determine the oxygen and sulfur valence angles by application of the same method to ethers and sulfides, although the treatment is complicated by the considerable moments between the carbons and the oxygen or sulfur atoms. At the same time it appears desirable to consider the moments of certain newly determined heterocyclic compounds together with those of closely related compounds in the literature.

Preparation of Materials

Benzene and heptane were prepared as previously described.[1] The other materials, except as noted, were obtained from the Eastman Kodak Company. The densities and refractive indices determined for the liquids are given as criteria of purity.

***p*-Bromoanisole.**—Material (m. p. 12–13°) was dried with anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 101.9–102.1° (18 mm.); n_D^{20} 1.56422; n_D^{25} 1.56212; d_4^{25} 1.4902; d_4^{50} 1.4597.

***p*-Bromophenetole.**—Material (m. p. 2–4°) was dried with anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 109.2–109.5° (17 mm.); n_D^{20} 1.55168; n_D^{25} 1.54950; d_4^{25} 1.4071; d_4^{50} 1.3768.

***p*-Bromodiphenyl Ether.**—Material (b. p. 167–168° (15 mm.)) was dried with anhydrous sodium sulfate and fractionally distilled under reduced pressure; b. p. 171.6–171.7° (17 mm.); d_4^{25} 1.4155; d_4^{50} 1.3896.

4,4′-Dibromodiphenyl Ether.—Material (m. p. 57.5–58.5°) was twice fractionally crystallized from petroleum ether and dried in a vacuum desiccator; m. p. 58.8–58.9°.

4,4′-Dinitrodiphenyl Ether.—Material which had been recrystallized from alcohol, partially decolorized with norit, and finally crystallized from benzene, and had a m. p. 142–143°, was further purified by repeated treatments with "Darco" in benzene solution. After being twice fractionally crystallized from benzene and dried in an evacuated desiccator, it had only a very faint yellowish tinge, which could not be removed by further treatment with decolorizing materials; m. p. 144.4–144.7°.

4,4′-Dibromodiphenyl Sulfide.—Material, prepared by Mr. P. D. Hammond and kindly loaned for our measurements, had been purified by crystallization from glacial acetic acid and drying in a vacuum desiccator to remove acetic acid; m. p. 112.2–112.4°. This material was twice fractionally crystallized from a mixture of benzene and petroleum ether, washed with petroleum ether, and dried in a vacuum desiccator; m. p. 112.6–112.8°.

[1] Smyth and Walls, THIS JOURNAL, **54**, 1854 (1932).

Divinyl Ether.—Material[2] loaned by Dr. W. L. Ruigh of the Laboratory for Pure Research of Merck and Company, Inc., was dried over sodium wire and fractionally distilled; b. p. 28.31 ± 0.03° (758.7 mm.); n_D^{20} 1.39892.

Furan.—Material obtained from the Miner Laboratories, Chicago, was purified by fractional distillation through a soda lime tower as described in "Organic Syntheses," Vol. VII, p. 40 (New York, John Wiley and Sons, Inc., 1927); b. p. 31.3° (757 mm.); n_D^{20} 1.42150; n_D^{25} 1.41852; d_4^{20} 0.9378; d_4^{25} 0.9313.

Tetrahydrofuran.—This was prepared under the direction of Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company by catalytic reduction of the above described furan in butyl alcohol solution. It was purified by fractional distillation through a 1.8-meter fractionating column, dried with anhydrous sodium sulfate, decanted and fractionally distilled; b. p. 64.0–64.1° (755 mm.); n_D^{20} 1.40550; n_D^{25} 1.40355; d_4^{20} 0.8966; d_4^{25} 0.8910; d_4^{50} 0.8631.

Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the non-polar were measured with the apparatus and methods previously employed,[1,3] a wave length of 1000 meters being used in the dielectric constant determinations. In Table I the first column gives the

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Benzene–*p*-Bromoanisole			
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01723	2.402	2.338	.8882	.8610	141.6	135.3
.02893	2.488	2.416	.8984	.8712	140.4	135.0
.04318	2.591	2.508	.9105	.8833	138.3	132.9
.06374	2.738	2.639	.9273	.9003	135.6	130.2
.06900	2.776	2.672	.9317	.9046	135.0	129.6
.09091	2.929	2.809	.9493	.9225	132.1	127.0
			Heptane–*p*-Bromoanisole			
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.02183	2.013	1.967	.6950	.6730	148.2	141.8
.04528	2.114	2.058	.7115	.6893	145.7	139.3
.06302	2.191	2.128	.7239	.7017	143.8	137.7
.07361	2.238	2.169	.7317	.7091	142.6	136.5
.10479	2.375	2.293	.7542	.7313	139.0	133.6
.14445	2.549	2.452	.7831	.7597	134.4	130.1
			Benzene–*p*-Bromophenetole			
0.00000	2.278	2.228	0.8734	0.8465	(26.70	26.78 = P_1)
.01124	2.371	2.311	.8830	.8557	161.9	155.8
.02059	2.449	2.381	.8910	.8638	160.3	154.5
03451	2.565	2.483	.9023	.8751	158.2	152.3
.05200	2.706	2.611	.9167	.8893	155.4	149.7
.07009	2.850	2.738	.9310	.9035	152.4	146.8
.09847	3.072	2.936	.9531	.9254	148.0	142.9

[2] Ruigh and Major, THIS JOURNAL, **53**, 2662 (1931).

[3] Smyth and Walls, *ibid.*, **53**, 527 (1931).

TABLE I (*Continued*)

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Heptane–*p*-Bromophenetole			
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.02289	2.030	1.983	.6958	.6740	167.8	160.9
.03849	2.105	2.051	.7068	.6849	165.3	158.8
.06489	2.233	2.168	.7259	.7036	161.3	155.7
.10200	2.413	2.331	.7524	.7297	156.3	151.1
.13172	2.558	2.464	.7738	.7509	152.4	147.8
			Benzene–*p*-Bromodiphenyl Ether			
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01589	2.342	2.286	.8905	.8636	111.7	108.6
.03227	2.408	2.349	.9080	.8810	111.0	109.2
.04916	2.476	2.410	.9251	.8981	110.9	108.5
.07661	2.581	2.507	.9515	.9246	110.0	107.7
.10200	2.674	2.597	.9750	.9480	109.0	107.5
			Heptane–*p*-Bromodiphenyl Ether			
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.01919	1.972	1.931	.6969	.6750	116.9	113.8
.04042	2.030	1.986	.7158	.6938	116.7	114.5
.07109	2.114	2.063	.7431	.7209	115.6	112.8
.11641	2.240	2.178	.7825	.7600	113.9	110.9
			Benzene–4,4′-Dibromodiphenyl Ether			
0.01144	2.293	2.242	0.8942	0.8669	76.5	76.6
.01656	2.299	2.248	.9031	.8758	76.2	75.7
.02482	2.310	2.260	.9177	.8903	75.8	76.3
.03307	2.321	2.271	.9316	.9040	76.3	76.7
.04389	2.335	2.284	.9498	.9221	76.4	76.2
.06571	2.362	2.313	.9848	.9571	76.4	76.8
			Heptane–4,4′-Dibromodiphenyl Ether			
0.01555	1.939	1.902	0.7018	0.6801	75.1	74.5
.02773	1.952	1.914	.7174	.6954	76.4	75.5
.03367	1.960	1.922	.7253	.7033	77.7	76.5
.04351	1.972	1.934	.7388	.7165	77.6	76.9
.04543	1.974	1.936	.7415	.7193	77.3	76.4
			Benzene–4,4′-Dinitrodiphenyl Ether			
0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.00202	2.299	2.246	.8757	.8488	224.7	209.9
.00308	2.311	2.257	.8770	.8500	221.5	211.8
.00343	2.315	2.260	.8773	.8503	222.0	210.4
.00473	2.330	2.274	.8788	.8518	221.2	210.6
.00482	2.330	2.274	.8789	.8519	217.6	209.3
.00596	2.342	2.286	.8803	.8533	214.6	209.6
.00690	2.352	2.295	.8812	.8542	213.1	207.9
.00983	2.381	2.322	.8846	.8575	210.8	203.7

TABLE I (*Concluded*)

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Benzene–4,4′-Dibromodiphenyl Sulfide			
0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.00833	2.290	2.240	.8891	.8620	85.5	85.6
.00839	2.290	2.240	.8893	.8623	85.1	85.1
.01240	2.297	2.247	.8967	.8696	84.7	85.6
.01724	2.305	2.255	.9055	.8785	84.7	84.7
.02169	2.314	2.263	.9137	.8866	85.7	85.3
.02556	2.319	2.269	.9207	.8935	84.6	85.0
.02979	2.326	2.276	.9283	.9011	84.7	84.8
.03075	2.329	2.278	.9300	.9027	85.2	85.3
.03692	2.335	2.285	.9410	.9138	86.0	86.1
.04079	2.345	2.295	.9477	.9205	85.0	85.1
			Benzene–Furan			
0.0000	2.276		0.08734		(26.68 = P_1)	
.0286	2.289		.8748		28.4	
.0608	2.306		.8763		28.8	
.0664	2.308		.8765		28.8	
.1338	2.340		.8796		28.6	
.1355	2.341		.8797		28.6	
.1731	2.363		.8816		28.8	
1.0000	2.953		.9313		28.8	
			Benzene–Tetrahydrofuran			
0.00870	2.314	2.258	0.8737	0.8467	85.3	79.6
.00888	2.315	2.259	.8737	.8468	86.4	79.7
.01040	2.322	2.266	.8737	.8468	86.3	81.6
.01770	2.357	2.296	.8739	.8471	88.8	83.3
.01887	2.365	2.303	.8739	.8472	90.8	85.0
			1,4-Dioxane–Tetrahydrofuran			
0.00000	2.261	2.214	1.0312	1.0027	(25.27	25.30 = P_1)
.01778	2.347	2.291	1.0314	1.0028	87.2	83.7
.01898	2.352	2.296	1.0313	1.0027	87.0	83.3
.03259	2.419	2.355	1.0295	1.0010	87.9	83.9
.05522	2.533	2.454	1.0264	0.9978	87.8	83.6
.07986	2.660	2.569	1.0230	0.9944	87.3	83.8
	20°		20°		20°	
			Benzene–Divinyl Ether			
0.00000	2.286		0.8786		(26.65 = P_1)	
.04185	2.340		.8742		45.77	
.07059	2.380		.8712		46.06	
.09017	2.406		.8692		45.95	
.11617	2.443		.8666		46.02	
.14231	2.479		.8638		45.97	
.17611	2.527		.8602		45.96	
.22112	2.593		.8556		45.96	
1.00000	3.942		.7722		44.91	

mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ, the densities d of the solutions and the polarizations P_2 of the polar substance. The values of the molar refraction MR_D and of the moment μ in Table II were obtained as in previous papers.[1]

TABLE II

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	Solvent	MR_D	$P_\infty - MR_D$ 25°	50°	$\mu \times 10^{18}$ 25°	50°
p-Bromoanisole	Benzene	40.70	103.1	97.3	2.23	2.25
	Heptane		110.3	102.8	2.30	2.31
p-Bromophenetole	Benzene	45.47	118.1	111.8	2.38	2.41
	Heptane		125.7	117.9	2.46	2.48
p-Bromodiphenyl ether	Benzene		50.6	47.7	1.56	1.58
	Heptane	61.8[a]	56.4	53.5	1.65	1.67
4,4′-Dibromodiphenyl ether	Benzene	69.0[a]	7.4	7.5	0.60	0.62
	Heptane		8.1	7.4	0.62	0.62
4,4′-Dinitrodiphenyl ether	Benzene	65.5[a]	162.0	150.0	2.79	2.80
4,4′-Dibromodiphenyl sulfide	Benzene	76.5[a]	8.7	8.7	0.65	0.67
Divinyl ether	Benzene	21.94[b]	24.0[b]		1.06[b]	
Furan	Benzene	18.43	10.4		0.71	
Tetrahydrofuran	Benzene	19.76	60.9	56.2	1.71	1.71
	1,4-Dioxane		67.8	64.0	1.81	1.83

[a] Calculated from refractive indices and densities of solutions. [b] Measurements made at 20°.

Discussion of Results

It is interesting to note in Table II that the moments found for *p*-bromoanisole, *p*-bromophenetole and *p*-bromodiphenyl ether in benzene solution are 0.07–0.09 $\times 10^{-18}$ lower than the values found in heptane solution, which is the reverse of the situation in the case of the ethylene halides treated in a previous paper.[4] The differences are so small, however, that the conclusions to be drawn are not materially affected by using only the values obtained in benzene, which was a better solvent for the larger molecules and which was generally used in the measurements taken from the literature. The low values for 4,4′-dibromodiphenyl ether and the corresponding sulfide may be, at least, 0.2 $\times 10^{-18}$ too high because of neglect of the atomic polarization in the calculation. The P_2–c_2 curve for tetrahydrofuran in benzene is very different from that in dioxane, but the value found for the moment in benzene is but slightly lower. Its use, rather than that of an average value, will not affect the conclusions to be drawn.

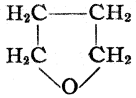
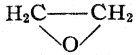
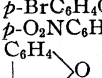
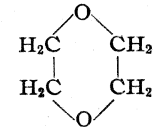
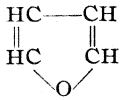
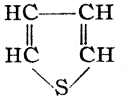
The values adopted for the moments and those taken from the literature[5] for use in calculation or discussion are listed in Table III.

[4] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

[5] See Smyth, "Dielectric Constant and Molecular Structure," New York, The Chemical Catalog Company, Inc., 1931, Appendices I and II.

TABLE III

ELECTRIC MOMENTS ($\times 10^{18}$)

C_6H_5Cl	1.52	$C_6H_5OCH_3$	1.2		
C_6H_5Br	1.50	*p*-$ClC_6H_4OCH_3$	2.24		
$C_6H_5NO_2$	3.9	*p*-$BrC_6H_4OCH_3$	2.24		1.71
H_2O	1.85	*p*-$O_2NC_6H_4OCH_3$	4.36		
H_2S	0.95	$C_6H_5OC_2H_5$	1.0		
$(CH_3)_2O$	1.29	*p*-$BrC_6H_4OC_2H_5$	2.40		
$(C_2H_5)_2O$	1.12	C_6H_5OH	1.70		
$(CH_2{=}CH)_2O$	1.06	*p*-ClC_6H_4OH	2.68		1.88
C_2H_5OH	1.70	*p*-BrC_6H_4OH	2.86		
C_2H_5SH	1.39[6]	*p*-$O_2NC_6H_4OH$	5.05		
$(C_2H_5)_2S$	1.57[6]				
$(C_6H_5)_2O$	1.05				
(*p*-$BrC_6H_4)_2O$	0.6		0.9		0.4
(*p*-$O_2NC_6H_4)_2O$	2.80				
p-$BrC_6H_4OC_6H_5$	1.57				
$(C_6H_5)_2S$	1.47				
(*p*-$BrC_6H_4)_2S$	0.6				0.6
p-$ClC_6H_4SC_6H_5$	1.76		0.7		

The method of calculating the oxygen valence angle θ is obvious from consideration of Fig. 1. The calculation is somewhat complicated by the presence of the dipoles in the directions of the C–O bonds and it is necessary to assume that these moments, as well as θ, are unaffected by the moments in the bonds of the para-substituted groups and *vice versa*. The validity of this assumption has been discussed in the previous paper dealing with the carbon valence angle, where it seems fully justified by the results. It may be a more inexact approximation in the case of the ethers and sulfides, where the C–O and C–S moments are immediately adjacent to the ring. Our ignorance of the absolute value of the small moment probably existing in the C–H bond causes no error in the calculations since it cancels out when a set of simultaneous equations for the moments involved in the diphenyl ethers is solved. This is apparent in the following calculation given as an example.

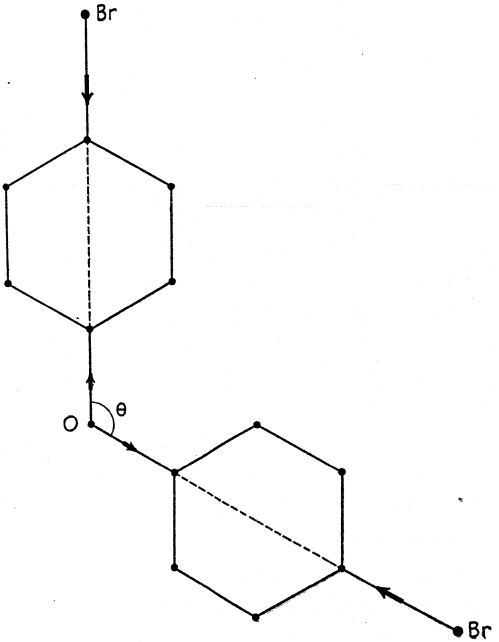


Fig. 1.—The 4,4′-dibromodiphenyl ether molecule.

[6] Hunter and Partington, *J. Chem. Soc.*, 2062 (1931).

$$C_6H_5Br \quad m_{C-H} + m_{C-Br} = 1.50 \times 10^{-18} \quad (1)$$
$$(C_6H_5)_2O \quad 2(m_{C-H} + m_{C-O}) \cos\theta/2 = 1.05 \times 10^{-18} \quad (2)$$
$$(p\text{-}BrC_6H_4)_2O \quad 2(m_{C-Br} - m_{C-O}) \cos\theta/2 = 0.6 \times 10^{-18} \quad (3)$$

Adding (2) and (3) and substituting (1), we have

$$3.00 \cos\theta/2 = 1.65, \text{ whence } \theta = 113°$$

In the cases of the monosubstituted ether and sulfide, the equation for the resolution of two unequal vectors has, of course, to be used. The angles calculated for oxygen and sulfur in the diphenyl ethers and sulfides by this method are given in Table IV.

TABLE IV

VALENCE ANGLES OF OXYGEN AND SULFUR

$(p\text{-}BrC_6H_4)_2O$	113°	$(p\text{-}BrC_6H_4)_2S$	146°
$p\text{-}BrC_6H_4OC_6H_5$	124°	$p\text{-}ClC_6H_4SC_6H_5$	147°
$(p\text{-}O_2NC_6H_4)_2O$	**121°**		

The angle calculated for $p\text{-}BrC_6H_4OC_6H_5$ is obtained by using the values of $(m_{C-H} + m_{C-O})$ and $(m_{C-Br} - m_{C-O})$ given by equations (2) and 3). The difference between the values of the angle for the monobromo and the dibromo ether is without significance. If the moment of the latter is taken as 0.4×10^{-18}, which may be more nearly correct than 0.6×10^{-18}, the angles calculated rise to 123 and 129°. The mean of these four rough values happens to be 122°, in excellent agreement with the value for $(p\text{-}O_2NC_6H_4)_2O$, which, being calculated from a large moment, is much more accurate than the others. If the presence of the nitro group increased the C–O moment by 0.15×10^{-18}, the value of θ would be lowered by only 3°, while, if the nitro group moment were increased at the same time, the lowering of the value calculated for θ would be less.

When $(p\text{-}BrC_6H_4)_2S$ is treated like the ether, a value of 98° is obtained for the sulfur valence angle, but, in the monochloro compound, the impossible value of -2 is obtained for $\cos\theta$. It, therefore, becomes necessary to suppose that m_{C-S} is greater than m_{C-Br}, that is $(m_{C-Br} - m_{C-S})$ is negative. The large angles given in Table IV are then obtained, the negligible difference between the moment of C_6H_5Cl, and that of C_6H_5Br being disregarded. If the moment of $(p\text{-}BrC_6H_5)_2S$ is taken as 0.5×10^{-18} instead of 0.6×10^{-18}, the angles calculated are 142 and 140°. The value calculated by Bergmann, Engel and Sándor[7] from their determination for $p\text{-}ClC_6H_4SC_6H_5$, which is the one here used, is 142°. When the equations used in calculating are solved for $m_{C-H} + m_{C-S}$, the value 2.5×10^{-18} is obtained, which is surprisingly high in comparison with the approximate figure 1.1×10^{-18} for $m_{C-H} + m_{C-O}$. This high value is not, however, irreconcilable with the moments of other sulfur compounds. The moment of the hydrogen sulfide molecule is little more than half that of the water

[7] Bergmann, Engel and Sándor, *Z. physik. Chem.*, [B] **10**, 397 (1930).

molecule, but replacement of hydrogen by an alkyl group in the sulfur compound raises the moment, while the moment is lowered by a similar change in the case of the oxygen compound. This is evident in the results of Hunter and Partington,[6] in Table III, which are in excellent agreement with values calculated by one of the writers.[8] If the value of the moment of p-$ClC_6H_4SC_6H_5$ obtained by Bergmann, Engel and Sándor is correct and if, as has been assumed, the moment of the para-substituted group is approximately independent of the other moments in the molecule, the large value of about 146° must be accepted for the sulfur valence angle in these diphenyl sulfides.

As methyl and ethyl ethers, anisole, phenetole and diphenyl ether have moments of the same magnitude, it is natural to suppose that the valence angles and the R–O moments in all these compounds are much the same whether R is an alkyl or a phenyl group. However, the moments of the para-halogenated anisoles and phenetoles are much higher than that of p-bromodiphenyl ether and it is impossible to calculate their moments on the basis of these assumptions. Actually, the alkyl halides have moments from $0.3–0.5 \times 10^{-18}$ higher than the phenyl halides. If the R–O moment when R is an alkyl group is taken as 1.8×10^{-18} as compared to a value of 1.1×10^{-18} obtained for R–O from the phenyl ethers, oxygen valence angles lying between 130 and 140° are obtained for the anisoles, methyl ether and the hydroquinone ethers, the equation for rotating dipoles being used in these latter calculations, and still larger angles are obtained for the phenetoles and ethyl ether. A larger angle in the phenetoles gives a lower moment to the unsubstituted compound and a higher one to the substituted as observed. If the H–O moment in the phenols is taken as 2.4×10^{-18}, instead of 1.6×10^{-18} as used by Eucken and Meyer,[9] the oxygen valence angles in the unsubstituted and in the p-chloro- and p-bromophenols are calculated as having values from 127 to 141°, the angle in p-nitrophenol being 152°. This H–O value gives a valence angle of 134° for water and, combined with the R–O value, 1.8×10^{-18}, an oxygen angle of 136° in the alcohols, the mutual inductive effects being neglected in both cases.

The difference between the phenyl R–O moment and the value assigned to that of the alkyl R–O is greater than would be expected. The experimental data on the anisoles and phenetoles are satisfactory, as evidenced, for example, by the identity of the value for p-bromoanisole obtained in the present investigation with that for p-chloroanisole obtained by Bergmann, Engel and Sándor.[7] Impurities, which might be present in small quantities only, should tend to lower the apparent values of the moments and thus make the difference between these substances and the diphenyl

[8] Smyth, THIS JOURNAL, **46**, 2151 (1924).

[9] Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

ethers appear less. The necessary neglect of the atomic polarization tends to make all the values a little high, but should not affect their comparison with one another or seriously alter the values of the angles calculated. It is evident that the moments of the substituted phenols are practically useless as a means of calculating the oxygen valence angle, possibly because of a shift to a quinoid structure. An example of this is probably found in *p*-nitroaniline, which has a moment, 7.1×10^{-18},[10] larger than the sum of the nitro and the amino moments acting in the same direction. The transmission of a large inductive effect through the ring could account for these discrepancies in the molecules which have two unlike groups attached to the oxygen, perhaps causing the apparent difference between the phenyl and the alkyl R–O moments. The transmission of such large effects appears consistent with chemical behavior but difficult to reconcile with the mutual independence of simple dipoles in meta- and para-disubstituted benzenes as summarized in the treatment of the carbon valence angle.[1] If such transmission were to occur from the two like substituents in the *p*,*p'*-disubstituted diphenyl ether, the two transmitted effects would so cancel each other as greatly to reduce the error caused in the calculated valence angle. In view of the uncertainty as to the interpretation of the data for the anisoles and phenetoles, it may be concluded only that there is an indication of the possibility of an oxygen valence angle larger than that found in the diphenyl ethers. It is obvious that the values used for the H–O and alkyl R–O moments cannot be regarded as determinations of these quantities.

If, in diphenyl ether, the C–C nuclear separation in the ring is taken as 1.42 Å.,[11] the C–O distance as 1.43 Å. and the C–H distance as 1.06 Å.,[12] and the hydrogen nuclei are assumed to be surrounded by repulsive spheres of radius 1.20 Å., calculation shows that, if the two benzene rings lay in the same plane, the oxygen valence angle would be widened to 169°. Indeed, with the rings in the same plane and an oxygen angle of 114°, the protons in the ortho position would be coincident. As the most reliable determination of this angle in the diphenyl ethers gives approximately 121°, it appears probable that the two rings oscillate about positions of minimum potential energy in which their planes are perpendicular to that of the oxygen valence angle.

In diphenylene oxide, if the external valences of the benzene rings made 120° angles with the adjacent sides of the hexagon in the normal fashion, the five-membered ring would be so distended that the C–O–C distance would be 2.99 Å. even if the oxygen valence angle were widened to 180°.

[10] Höjendahl, *Physik. Z.*, **30**, 391 (1929).

[11] Lonsdale, *Proc. Roy. Soc.* (London), **123**, 494 (1929); Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

[12] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

As this is more than double the C–O distance of 1.43 Å., it is evident that the carbon valence angles in this ring must be reduced below 120°, while the oxygen angle must be widened probably to more than 130°. As the force required to stretch a bond is much greater than that required to bend it, tension in the ring should be reduced more by alteration of the angles than by change of the internuclear distances, although both presumably occur. An exact quantitative treatment of this and of similar moments is impossible because of our ignorance of the size of effects, such as the adjustment of angles to lessen the ring tension, the stretching of bonds, the effect of such stretching upon bond moments, the size of the C–H dipoles and the angles which they make with the other parts of the molecule, but it is evident that the moment is markedly lower than those of ethyl, vinyl and phenyl ethers, as would be expected from the widening of the oxygen angle. If the furan ring were regarded as containing two double bonds, the carbon valence angles in the ring should tend to be 125°,[13] which would mean an even greater widening of the oxygen valence angle than in diphenylene oxide, perhaps to more than 140°, and a correspondingly lower moment, as observed. Since, however, the molar refraction MR_D, found for furan is 0.7 lower than the value calculated for it on the assumption of the occurrence of two double bonds in the ring, this simple explanation of the low moment is highly speculative.

The angle in a regular pentagon is 108°, but, in tetrahydrofuran, the fact that the C–O distance is about 1.43 Å. and the C–C about 1.54 Å. necessitates an alteration of the angles. It is impossible to say precisely what the oxygen angle is, but geometrical considerations indicate that it is probably not far from 100°, which causes the moment to be much higher than in the unsubstituted oxides previously discussed. As tetrahydrofuran is radically different in properties from furan, it may be that the disappearance of unsaturation also contributes to the increase in moment. This would accord with the assignment of a higher moment to the alkyl R–O. If the interatomic distances remain unchanged in the triangular ethylene oxide molecule, the oxygen valence angle is 65°, and the carbon angles in the ring 57.5°, which necessitates a higher moment than that of tetrahydrofuran, as observed, although the difference is less than would be expected. The very small moment, indistinguishable from zero, of dioxane indicates that the structure conforms to a symmetrically distorted hexagonal model with the four carbons in a plane and one oxygen above and the other below. The very small moment of thiophene shows a structure analogous to that of furan with a large sulfur valence angle of possibly 140° or more.

The heterocyclic compounds which have been discussed show the wide variation which the oxygen valence angle may be forced to undergo, from

[13] This angle would result if the double bond were formed by the sharing of an edge between two regular tetrahedra. *Cf.* Slater, *Phys. Rev.*, **37**, 481 (1931).

65° to, perhaps, 140°. Because of the fact that the effects upon one another of the different moments in the molecule may not be wholly negligible, as well as because of the experimental error, the oxygen valence angle in the diphenyl ethers cannot positively be taken as 121°. However, the previously advanced reasons for deciding these effects to be small are sufficient to warrant the conclusion that the angle is correct to within ±5°. It is evident that the 90° angle calculated by the wave mechanics[14] may be much altered by the groups with which the oxygen combines.

Summary

The electric moments of para-substituted diphenyl ethers and a sulfide, an anisole, a phenetole and heterocyclic compounds have been determined and used, together with other moments taken from the literature, to study the angles between the valences in the oxygen and sulfur atoms.

The oxygen valence angle in the diphenyl ethers is found to be 121 ± 5°. The results for the anisoles and phenetoles, which are more complex, do not give dependable values for the oxygen angle, although they may be explained in terms of an oxygen angle not far from 135°. Limited data give for the sulfur valence angle in the diphenyl sulfides a value of about 146°, which may be too high. The oxygen valence angles in various heterocyclic compounds calculated from the interatomic distances vary from 65 to about 140° and the moments are in excellent qualitative agreement with predictions based on the size of the angles. The behavior of thiophene is strictly analogous to that of the corresponding oxygen compound.

[14] Slater, *Phys. Rev.*, **37**, 481 (1931); *ibid.*, **38**, 1109 (1931); Pauling, THIS JOURNAL, **53**, 1367 (1931).

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE ACTION OF HYDRIODIC ACID ON STANNIC OXIDE

BY EARLE R. CALEY

RECEIVED MAY 5, 1932 PUBLISHED AUGUST 5, 1932

The recent note of Laubengayer and Brandt[1] on a method for the preparation of germanium tetraiodide by the action of hydriodic acid on germanium dioxide leads me to mention an analogous reaction that I first observed some months ago and to which I can find no reference in the chemical literature.

It is a well-known fact that stannic oxide, especially ignited stannic oxide, is very resistant toward the usual chemical reagents. It was found, however, that concentrated hydriodic acid acts readily on stannic oxide, converting the latter into stannic iodide. With constant boiling hydriodic acid the reaction commences at about 90–95° and takes place quite

[1] Laubengayer and Brandt, THIS JOURNAL, **54**, 621 (1932).

rapidly at the boiling point of the acid. The conversion is never quite complete with fixed amounts of the reactants in a closed system but successive additions of hydriodic acid to a heated reaction mixture will effect the complete transposition of the stannic oxide. With slightly diluted acid the reaction is slower and less complete, while dilute hydriodic acid has no effect. Stannic oxide prepared by different methods and ignited at various elevated temperatures gives the same reaction. Even the natural oxide, when powdered, reacts readily with concentrated hydriodic acid in the manner described.

The following experiments were performed to establish the course of the reaction.

A. On heating a weighed amount of stannic oxide with hydriodic acid, the increase in weight, after allowing for the amount of oxide not acted upon and after removal of the excess acid, was found to correspond closely to the calculated increment for the formation of stannic iodide alone. In a typical experiment 0.1553 g. of pure stannic oxide, prepared by igniting the metastannic acid derived from a specimen of Kahlbaum's pure tin, was placed in a weighed glass dish together with 3.0 cc. of pure constant boiling hydriodic acid. After heating the covered vessel for fifteen minutes on a steam-bath the dish was placed in a desiccator charged with calcium chloride, potassium hydroxide and metallic copper to remove water, excess acid and iodine formed by the oxidation of the hydriodic acid. Simple evaporation of the excess hydriodic acid by heating was found to be an impossible procedure for exact work, due to the volatility of the stannic iodide under these conditions. After reaching constant weight, the contents of the dish were found to weigh 0.5672 g. The tin iodide in the mixture was dissolved out with pure benzene, leaving a residue of unchanged stannic oxide weighing 0.0249 g. From these data it follows that 0.1304 g. of oxide was converted into 0.5423 g. of iodide. This agrees well with the calculated value of 5420 g. based upon the conversion of the stated amount of oxide into stannic iodide alone.

B. Analysis of the salt obtained by evaporation of the benzene extracts from experiments like the one just described indicated that stannic iodide was the sole compound present.

Anal. Sample taken, 0.4857 g.: SnO_2 found, 0.1175 g.; AgI found, 0.7283 g.; Sn, 19.06%; I, 81.06%; total, 100.12%. Another specimen was analyzed for tin by an alternative method: sample taken, 0.2594 g.; SnO_2 found, 0.0626 g.; Sn, 19.01%. Calculated for SnI_4: Sn, 18.95%; I, 81.05%.

C. On heating the two reacting substances under an atmosphere of carbon dioxide no iodine was found to be liberated from the reaction, thus indicating absence of valence change.

D. The salt obtained from the reaction hydrolyzed slowly on the addition of water in accordance with the known behavior of stannic iodide.

On the basis of these experiments it follows that the reaction may be represented by the simple equation

$$SnO_2 + 4HI \rightleftharpoons SnI_4 + 2H_2O$$

This reaction is therefore quite analogous to the one between germanium dioxide and hydriodic acid and it differs from the general one between this acid and most higher metallic oxides.

In contrast to the chemical action of hydrobromic acid on germanium dioxide as recorded by Laubengayer and Brandt,[1] stannic oxide is apparently not affected by hot concentrated hydrobromic acid. Several experiments in which different specimens of stannic oxide were heated with many times their weight of constant boiling hydrobromic acid yielded no evidence of any action between the two substances. In a typical quantitative experiment, for example, 0.2170 g. of pure ignited stannic oxide treated with 10 cc. of hydrobromic acid at the steam-bath temperature for an hour left a residue of stannic oxide weighing 0.2169 g. after evaporation of the acid. There is, therefore, an interesting and distinct difference in the behavior of these two related oxides toward hydrobromic and hydriodic acids.

The formation of red stannic iodide in the manner described is a rather distinctive reaction for stannic oxide and can serve to differentiate readily this latter substance from other highly insoluble compounds encountered in qualitative analysis. It also suggests itself as a convenient means for identifying the natural oxide, cassiterite. If pure constant boiling hydriodic acid is employed in making the test, however, liberation of iodine is often so excessive that the reaction is obscured unless it is performed under a carbon dioxide atmosphere. It is much preferable for this purpose to use the concentrated acid that has been stabilized by the addition of 1–2% of hypophosphorous acid. A reagent of this composition behaves like the pure acid toward stannic oxide, can be kept without decomposition, and permits the performance of the test in air since liberation of iodine is slight even at the boiling point. In making the test it is sufficient to treat the powdered sample with a few cc. of the above reagent and boil the mixture gently in a test-tube for two or three minutes. In the presence of stannic oxide the orange-red stannic iodide is formed in the reaction mixture and on the cooler parts of the vessel it appears as a yellow to orange sublimate. With proper manipulation amounts of oxide as small as one milligram can be readily identified.

Summary

1. Concentrated hydriodic acid readily reacts with stannic oxide forming stannic iodide and water.

2. Concentrated hydrobromic acid does not react with stannic oxide under similar conditions.

3. The reaction described can be used as a qualitative test for natural or artificial stannic oxide.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

AN EQUATION FOR THE REPRESENTATION OF HIGH-TEMPERATURE HEAT CONTENT DATA[1]

BY CHAS. G. MAIER[2] AND K. K. KELLEY[3]

RECEIVED MAY 9, 1932 PUBLISHED AUGUST 5, 1932

High temperature heat content data have commonly been represented by the empirical equation

$$Q_{273.1}^{T} = \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \ldots\right]_{273.1}^{T} \qquad (1)$$

because the manipulation of such power series is easy and rapid. However, it is well known that this form of equation is not particularly satisfactory for the purpose. A reasonable number of terms often cannot be made to fit the data with sufficient accuracy; moreover, the resulting derived equation for specific heat

$$C_p = a + bT + cT^2 + \ldots\ldots \qquad (2)$$

may have a maximum in the temperature range under consideration due to the signs and magnitudes of the coefficients, but such a maximum does not correspond to known physical facts. These difficulties are most apparent where the specific heats are still far below the Dulong and Petit equipartition value of 6 calories per gram atom at 0°. Obviously, a better form of equation is desirable, but the choice is limited by several conditions: namely, (1) the equation selected should be usable in conjunction with conventionally accepted methods in thermodynamic calculations, (2) differentiation and integration under the conditions imposed by thermodynamic calculations should be analytic and reasonably easy to perform, and (3) derived values should be consistent with the available facts.

The Pacific Experiment Station of the United States Bureau of Mines is interested in the correlation of high temperature thermal data on metallurgically important elements and compounds, and has investigated several forms of equations for the representation of these data. It is apparent that at high temperatures specific heats of normally behaving substances

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Metallurgist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, Calif.

[3] Associate Physical Chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, Calif.

in the solid or liquid state increase nearly linearly with the temperature, and that a subtractive term is needed which will be effective at temperatures lower than that where the equipartition value of specific heat is reached. Consequently, the following equations are proposed

$$C_p = a + bT - cT^{-2} \quad (3)$$

$$Q_{273.1}^{T} = \left[aT + \frac{b}{2}T^2 + cT^{-1}\right]_{273.1}^{T} \quad (4)$$

The conditions mentioned above are satisfied by equation (4), and trial on the data for several substances has shown that it gives a satisfactory representation, as may be seen from the following examples.

The data on zinc oxide recently were reviewed by Maier,[4] who has represented the available figures by the expression

$$Q_0^t = 9.35t + 4.34 \times 10^{-3}t^2 - 1.574 \times 10^{-6}t^3$$

This equation is equivalent to

$$Q_{273.1}^{T} = [6.63T + 5.63 \times 10^{-3}T^2 - 1.574 \times 10^{-6}T^3]_{273.1}^{T} \quad (5)$$

based on the specific heat value 9.35 cal. per degree per gram formula weight at 0°, and the total heats obtained by White and Day[5] for 700 and 1300°. If equation (5) is differentiated, the resulting C_p equation has a maximum at 920°, which is without physical significance. Using the same three data for determining the constants in equation (4), there is obtained

$$Q_{273.1}^{T} = 11.40T + 0.726 \times 10^{-3}T^2 + 1.824 \times 10^{5}T^{-1} - 3835 \quad (6)$$

The comparison of equations (5) and (6) with the actual experimental data on zinc oxide is shown in Table I.

TABLE I

HEAT CONTENT OF ZINC OXIDE ABOVE 0°

Temp., °C.	Observed heat content	Observer	Equation (5)	Diff., %	Equation (6)	Diff., %
98	984	Regnault	957	−2.7	988	+0.4
99	995	Magnus	967	−2.8	998	+ .3
259	2886	Magnus	2686	−6.9	2780	−3.7
550	6033	Magnus	6193	+2.7	6262	+3.8
700	8132	White and Day	8132	0.0	8132	0.0
900	10677	White and Day	10783	+1.0	10692	+ .1
1100	13306	White and Day	13443	+1.0	13320	+ .1
1300	16009	White and Day	16009	0.0	16009	.0

It is seen that White and Day's data are represented with great exactness and furthermore that the agreement with the less accurate lower temperature data is very much better with equation (6) than with equation (5).

[4] Maier, U. S. Bureau of Mines Bulletin 324, "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," pp. 18–20.

[5] See Maier and Ralston, THIS JOURNAL, **48**, 364 (1926).

The heat content of calcium silicate in the form of pseudowollastonite has been measured by White[6] up to 1400°, and Parks and Kelley[7] have measured specific heats at low temperatures on the same sample. A smooth curve through the results of the latter investigators gives $C_{p,\ 273.1} = 20.06$ cal. per degree per gram formula weight, a value far removed from the equipartition figure of about 30. Using this datum and White's total heat figures at 700 and 1400°, the following expressions are obtained and a comparison is made in Table II.

$$Q^{T}_{273.1} = 12.82T + 14.90 \times 10^{-3}T^{2} - 4.020 \times 10^{-6}T^{3} - 4530 \quad (7)$$

$$Q^{T}_{273.1} = 25.48T + 2.066 \times 10^{-3}T^{2} + 4.881 \times 10^{5}T^{-1} - 8900 \quad (8)$$

TABLE II

HEAT CONTENT OF CALCIUM SILICATE ABOVE 0°

Temp., °C.	White's data	Equation (7)	Diff., %	Equation (8)	Diff., %
100	2140	2120	−0.9	2200	+2.8
300	7125	6950	−2.5	7230	+1.5
500	12600	12430	−1.3	12660	+0.5
700	18350	18350	0.0	18350	.0
900	24290	24530	+1.0	24250	− .2
1100	30390	30760	+1.2	30340	− .2
1300	36630	36870	+0.7	36610	− .1
1400	39800	39800	.0	39800	.0

Here, again, equation (8) is much more satisfactory than equation (7). At only one point, 100°, does equation (7) fit better, but this particular experimental value may be low, as the curve given by Parks and Kelley indicates.

The proposed equations are by no means perfect, but appear to be definitely better than the older forms; they require no additional data and are as easily handled as the ordinary power series expressions, in conjunction with which they readily may be used, if desired. Also, all the data investigated so far (which are for metals, oxides and silicates) are adequately represented by the three constant equations, there being no necessity for adding more terms, as is often the case when the power series expressions are used. It is preferable to obtain the constants in the manner indicated by solving simultaneously one specific heat equation, into which has been substituted the true specific heat at 273.1°K., and two total heat equations. This makes the resulting equations consistent with both the high temperature and low temperature thermal data. Where no true specific heat measurements exist, three total heat equations must be solved for the constants. No difficulty is encountered in writing heat of reaction and free energy equations, which are of the form

[6] White, *Am. J. Sci.*, [4] **28**, 334 (1909); **47**, 1 (1919).

[7] Parks and Kelley, *J. Phys. Chem.*, **30**, 1175 (1926).

$$\Delta H_T = \Delta H_0 + \Delta a T + \frac{\Delta b}{2} T^2 + \Delta c T^{-1} \quad (9)$$

$$\Delta F^\circ_T = \Delta H_0 - \Delta a T \ln T - \frac{\Delta b}{2} T^2 + \frac{\Delta c}{2} T^{-1} + IT \quad (10)$$

Summary

The equation $Q^T_{273.1} = \left[aT + \frac{b}{2} T^2 + cT^{-1}\right]^T_{273.1}$ is suggested for the representation of high temperature thermal data and is shown to be superior to the ordinary power series expression. The suggested equation is readily usable in all thermodynamic calculations, involves no additional labor and may be employed in conjunction with power series expressions, if desired.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

APPARATUS FOR QUANTUM YIELDS OF GAS REACTIONS BY ACTINOMETRY

BY GEORGE S. FORBES, GEORGE B. KISTIAKOWSKY AND LAWRENCE J. HEIDT

RECEIVED MAY 12, 1932 PUBLISHED AUGUST 5, 1932

By proper use of actinometry it is possible to avoid most of the difficulties of radiometric procedures, also the disadvantage that radiometric errors can be estimated only by the original investigator and only before his apparatus is dismantled. When quantum yields are referred to a reproducible standard under identical conditions, systematic errors tend to cancel out. If, later, the given actinometer is restandardized, it is easy to recalculate all quantum yields previously referred to it.

In this Laboratory the quantum yields of uranyl oxalate have been determined within 5% over the range 435 to 254 mμ,[1] also 278 to 208 mμ,[2] thus providing the basis for an advance in actinometric procedure. We have constructed an apparatus (Figs. 1, 2) for quantitative study of photochemical gas reactions attended by pressure changes. It could easily be modified for studies of gas reactions without pressure change, or of liquid systems.

Light from a vertical mercury vapor lamp O (Fig. 1) was resolved by the conventional train between the quartz condenser, Q_c, and the exit slit, E, cut to fit the image of the spectral line furnishing the monochromatic radiation. A shutter was placed between O and Q_c. A small elliptical quartz lens of short focus, Q_e, lessened the divergence of the issuing beam.

Two quartz cells, each the frustum of a rectangular pyramid, had identical dimensions and a volume approximately 40 cc. All seams were fused. The gas cell, C_g, shown in detail in Fig. 2, had a capillary inlet, I. The acti-

[1] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

[2] Brackett and Forbes, data to be published.

nometer cell, C_a, had instead a tubulure 4 mm. in internal diameter through which passed a small stirrer propelled by a windmill. Either cell enveloped the light beam diverging from E, just avoiding incidence of light upon the side walls. Each cell was encased in a copper jacket, J, having two rectangular openings, opposite the front and back windows. Copper ribbons

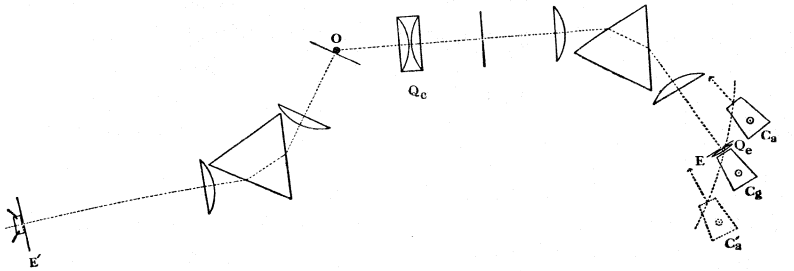
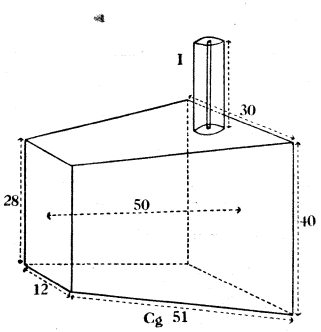


Fig. 1.

10 mm. wide soldered around the edges of these openings and cemented around the ends of the cells made the jackets water-tight. Thermal insulation was provided by cork sheets 6 mm. thick (1 mm. over the front wall). A cork cover insulated the rear window. Water from thermostats was circulated by pumps at a uniform rate through the jackets. The temperature of the issuing water remained constant within $\pm 0.05°$.



Dimensions in mm.

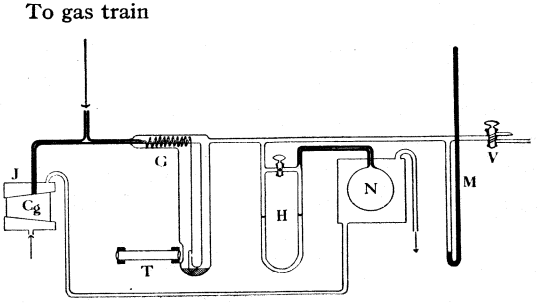


Fig. 2.

The apparatus to the right of O, Fig. 1, permits direct comparison of reaction rate in C_g with that in C_a by exposing the cells alternately behind E for measured times. Frequent shifting would average out lamp fluctuations, but this always is inconvenient, and would be unsuitable if the gas reaction involved induction periods or after effects. Therefore, we added a second monochromator in fixed position to the left of O. Its exit slit E′ receives the image of the *same* spectral line as is incident upon E. By means of the thermopile behind E′ and a high-sensitivity galvanometer,

scale deflections *proportional* to the energy flux emerging from either E′ or E can be measured frequently during an experiment. Such readings make it possible to separate short-time variations in photochemical reaction rate from simultaneous fluctuations in the lamp.

As C_g must be rigidly mounted, it cannot be removed to allow substitution of C_a. Therefore the train from Q_c to E was solidly mounted upon a horizontal steel plate 3 mm. thick (not shown) which slid freely upon the upper surfaces of three heavy steel bars held parallel to each other. By means of a rigid steel arm suitably bent the plate was pivoted directly under O. To shift radiation from C_g (Fig. 1) to C_a, E was first detached from the plate (all cell windows covered) and the plate swung through the required angle. Next E was attached again to the plate in front of C_a, and the beam accurately centered by means of a screw mechanism operated through a milled head. Exposure of C_a in two positions C_a and C_a' as shown (Fig. 1) made it possible to average out any error due to uneven spatial distribution in the radiation of the lamp.

Pressure changes in C_g were measured in the customary fashion in terms of an artificial atmosphere, using as a null instrument a Bodenstein quartz spiral gage, G, Fig. 2. An offset near the free end of the pointer dipped in triacetin and damped out vibrations. Observing the end of the pointer through the telescope, T, pressure differences of 0.05 mm. of mercury were readily recognized by the excursions of the pointer from the fixed zero point. The gage was connected to the reaction cell by a Pyrex capillary and two graded seals; the combined volume of these was less than five per cent. that of the cell. The Pyrex jacket surrounding the gage communicated with a compensation cell, N, of appropriate volume, thermostated at the same temperature as C_g. All parts of the compensating system not thermostated were wrapped with heavy felt; otherwise drafts produced erratic changes in the apparent pressure within C_g. Differences in pressure between C_g and N could be read from the triacetin manometer H, and total pressures (by cathetometer) from the mercury manometer M.

If the reaction is free from complications, the second monochromator is dispensed with, and C_g and C_a are exposed alternately behind E for measured times Δt_g and Δt_a. Repeating, C_a is exposed on the other side of C_g. While C_a is being exposed, the dark reaction, if any, is studied in C_g. Assume the ratio of total quanta received by C_g and C_a, respectively, equal to $\Sigma\Delta t_g/\Sigma\Delta t_a$, after suitable corrections for difference in the reflections quartz–gas and quartz–water, also for any transmissions exceeding one per cent. Then the quantum yield of the gas reaction $\phi_g = \phi_a \Delta m_g \Sigma\Delta t_a / \Delta m_a \Sigma\Delta t_g$ where Δm_g and Δm_a equal the moles transformed in C_g and C_a as measured by manometry and titration, respectively.

If the second monochromator is used, galvanometer deflections are frequently recorded during irradiations of C_g and C_a and plotted against the

corresponding times as ordinates. The cell C_a is exposed (using both positions) until the quantity of oxalic acid decomposed is measurable with the degree of precision desired. The area under the curve is divided into strips by ordinates at those times which mark the various stages of the experiments. The area of any strip is proportional to total quanta emerging from either exit slit during the corresponding time interval. Corrections for reflection and transmission are made as stated above. Let A_g be the area of the strip corresponding to a given exposure of C_g, and $(A_a + A'_a)$ the sum of the areas for the two exposures of C_a. Also let $\Sigma(h\nu)_g$ and $\Sigma(h\nu)_a$ be corrected total quanta absorbed, and Δm_g, Δm_a the moles transformed during the same time intervals. Then $\phi_g = \phi_a \Delta m_g \Sigma(h\nu)_a / \Delta m_a \Sigma(h\nu)_g = \phi_a \Delta m_g (A_a + A'_a) / \Delta m_a A_g$.

If the apparatus is carefully handled, the ratio $(A_a + A'_a)/\Delta m_a$ remains constant and reproducible within experimental error, and need not be rechecked for each refilling of the gas cell.

Summary

An apparatus and a method are described whereby the quantum yield of a photochemical gas reaction over any time interval during its progress may be stated in terms of the quantum yield of uranyl oxalate in monochromatic light of the same wave length with a probable error of five per cent.

CAMBRIDGE, MASSACHUSETTS

A NEW METHOD FOR THE DETERMINATION OF PROPIONIC ACID

BY JAMES B. MCNAIR

RECEIVED MAY 12, 1932 PUBLISHED AUGUST 5, 1932

There is a need for a suitable method for the quantitative estimation of propionic acid in the presence of formic and acetic acids. This becomes of special importance in connection with the analysis of acids produced by fungi. The fact that oxalic acid is produced by the following method from propionic acid but is not formed from formic and acetic acids under the same circumstances serves as a basis for a new method for the determination of propionic acid.

Method.—To every 5.94 cc. of 0.1 *N* propionic acid, 1.5 g. of anhydrous sodium carbonate, 17.5 cc. of 3.12% potassium permanganate, and 27 cc. of distilled water are added in a 250-cc. Pyrex Erlenmeyer flask. This flask is capped by a small glass beaker and the entire Erlenmeyer covered by a large glass beaker and placed on a steam-bath for four hours. After that time the Erlenmeyer is removed from the steam-bath and 5 cc. of 95% alcohol added to eliminate the excess potassium permanganate. The manganese dioxide is separated by filtering the mixture through an alundum crucible under suction. The alundum crucible is placed in a

funnel, the stem of which passes through the neck of a bell jar into a beaker. The crucible is washed five times with distilled water before and after filtering the manganese dioxide. The filtrate is now acidified with glacial acetic acid and 3 g. of calcium acetate added and let steam overnight. The precipitate (calcium oxalate) is collected on an alundum crucible by filtration and washed with four fillings of distilled water. The crucible and contents are now placed in a 250-cc. beaker. Ten cc. of concentrated sulfuric acid is added just before the final titration with 0.04 *N* potassium permanganate. During the titration the acid liquid is kept at a temperature of 65 to 70° and the titration with potassium permanganate continued until the rose tint remains permanent for two minutes.

Two check experiments required for each 5.94 cc. of 0.1 *N* propionic acid 18.60 and 18.60 cc., an equivalent of 7.44 of 0.1 *N* potassium permanganate.

It was found that with the above amounts of material the formation of oxalic acid was not complete with less than three hours of heating on the steam-bath. When experiments were first begun with this method the excess potassium permanganate was oxidized with hydrogen peroxide formed by the addition of sodium peroxide. All glassware used in the experiment had been cleaned with dichromate sulfuric acid cleaning mixture.

Summary

A new method has been described for the determination of propionic acid. In this method propionic acid is oxidized to oxalic acid. Such a method is especially valuable in the determination of propionic acid in the presence of formic and acetic acids.

818 South Ardmore Avenue
Los Angeles, California

[Contribution from the Chemical Laboratory of Harvard University]

THE ELECTRON AFFINITY OF FREE RADICALS. IV. COMPOUNDS NOT AROMATIC HYDROCARBONS

By H. E. Bent, M. Dorfman and W. F. Bruce

Received May 14, 1932 Published August 5, 1932

In the three previous papers of this series[1] values for the free energy change of the reaction of addition of sodium to eight organic free radicals have been reported and by combination with appropriate equations the electron affinities in the gaseous state calculated. These free radicals contained only phenyl, biphenyl or naphthyl groups attached to the trivalent carbon atom. The values of ΔF for the reaction[2]

[1] H. E. Bent This Journal, **52**, 1498 (1930); **53**, 1786 (1931); Bent and Dorfman, *ibid.*, **54**, 1393 (1932).

[2] The standard state is the metal in the case of the sodium and for the other species the activity is taken as equal to the mol fraction.

$$Na + R = Na^+ + R^- \quad (1)$$

in which R represents the free radical, were found to fall within narrow limits ranging from −17.9 kg. cal. for triphenylmethyl to −20.6 kg. cal. for tri-bi-phenylmethyl and within these limits the effects produced by the various groups were additive. The electron affinity in the gaseous state for these compounds was caclulated to be about 60 kg. cal.

That these compounds should all give nearly the same value of ΔF for this reaction is perhaps not very surprising in view of the fact that in each case an electron is being added to an "odd" molecule to complete an electron pair. In all of the compounds heretofore studied the central atom has been carbon and the three groups attached to this carbon have been aromatic in structure. It would seem very desirable to continue the study of this reaction, extending the work to compounds of non-aromatic structure.

Unfortunately the requirements of the problem greatly limit the number of compounds which may be studied. In the first place it is essential that the ethane be either largely dissociated into the free radical or else that the equilibrium constant for this dissociation be known. If neither of these conditions is satisfied, then the addition of sodium to the ethane involves not only the free energy change of the addition of sodium to the free radical but also the unknown free energy of dissociation of the ethane. Knowing the sum of these two values and either one, the other may be calculated. From the standpoint of this investigation it is necessary to know the free energy of dissociation of the ethane or else that this be nearly complete. The converse of this calculation, the determination of the dissociation of ethanes by measuring the equilibrium with sodium, is the subject of another investigation which will be reported later.

Another very obvious requirement of this investigation is that a true equilibrium be established free from side reactions. These conditions make it impossible to study a great many of those compounds which satisfy the first condition of being largely dissociated. In some cases the solubility is too small and in others the sodium reacts with some active part of the molecule.

The free radicals reported in this paper are diphenylanisylmethyl, trianisylmethyl, pentaphenylcyclopentadienyl, pentaphenylethyl, the oxygen free radical, 9-chloro-10-phenanthroanyl and the nitrogen free radical α,α-diphenyl-β-trinitrophenylhydrazyl. These compounds are known to be largely dissociated.

Diphenylanisylmethyl showed a similar behavior to triphenylmethyl and gave approximately the same value for the electron affinity. Tri-*p*-anisylmethyl and pentaphenylcyclopentadienyl failed to yield sodium derivatives that had even a slight solubility in ether and possibly these free radicals were decomposed by sodium amalgams. 9-Chloro-10-phenanthrol formed a monosodium derivative with 1% sodium amalgam but the sodium

was held too firmly to be removed by mercury sufficiently to be detected analytically. The nitrogen free radical α,α-diphenyl-β-trinitrophenylhydrazine was undoubtedly decomposed in ether by saturated sodium amalgam, even nitrobenzene being decomposed by this treatment. Pentaphenylethane reacted with sodium in liquid ammonia but failed to yield a sodium derivative that could be extracted with ether.

Experimental

Diphenylanisylmethyl.—Diphenylanisylmethylcarbinol was obtained from the Eastman Kodak Co. in the form of a brown sirup. The melting point reported for the pure carbinol is 82°.[3] 7.8 g. of the sirupy carbinol was dissolved in 35 cc. of absolute ether and a little calcium chloride added. The addition of hydrogen chloride gas produced a white precipitate of the chloride. Ether was added to make a total volume of 125 cc. which dissolved the precipitated chloride and none separated upon again treating with hydrogen chloride. After standing overnight and filtering, the solution was evaporated to 30 cc. and cooled to 0°. White crystals of the chloride separated. These were crystallized twice more from ether at 0° to yield 2.4 g. of chloride melting at 123°. The value previously reported is 122°.

Anal. Calcd. for $C_{20}H_{17}OCl$: Cl, 11.50. Found: Cl, 11.54, 11.31.

The apparatus and procedure used in making the equilibrium measurements have been previously described.[1]

Table I gives the experimental data for the equilibrium measurements. The column headed log K_2 gives the values of the equilibrium constant for equation (1). A dissociation constant for the sodium addition compound giving ions, of 10^{-4} has been assumed here as was done in the earlier papers of this series. The dissociation constant for the ethane has been taken as 10^{-2} based upon molecular weight determinations.[4]

The mean value of ΔF is -18.3 kg. cal., which is not very different from 17.9 kg. cal., the value found for triphenylmethyl.[1]

TABLE I

EQUILIBRIUM CONSTANTS FOR THE ADDITION OF SODIUM TO DIPHENYLANISYLMETHYL

G. atoms Na removed × 10^4	G. atoms Na left × 10^4	Moles of ether	G. atoms of mercury	Log K_2 $K_1 = 10^{-2}$ $K_3 = 10^{-4}$	Mean	$+\Delta F$ kg. cal.
0.613	0.854	0.138	2.70	13.54		
.279	.282	.178	2.67	13.45		
.511	1.117	.139	1.35	13.54		
.580	0.275	.169	5.05	13.23		
.727[a]	.511	.182	3.48	13.19		
	(.520) by titration				13.4	−18.3

[a] Compound treated with 40% amalgam.

The equilibrium constants obtained agree with each other as well as for any of the preceding compounds studied. However, a decided difference was noted in the color change when adding mercury. With sodium tri-

[3] Gomberg and Buchler, THIS JOURNAL, **45**, 217 (1923).

[4] Ref. 3, p. 220.

phenylmethyl it was possible to see a partial disappearance of the red color upon shaking with a large quantity of mercury. The ether solutions of the other compounds studied were so dark that even a ten-fold dilution could not be noted and shaking with the quantities of mercury used produced no color change that could be detected.

The ether solution obtained by treating the diphenylanisyl chloride with saturated amalgam had a red color about the same as that of sodium triphenylmethyl. A small quantity of mercury changed this to a yellow, practically the same as that of the free radical solution obtained by treating the chloride in ether solution with mercury. This apparently indicated a nearly complete removal of sodium from the addition compound for even a fifty-fold dilution of the red solution gave a color distinctly red-orange. From Table I, however, it is seen that the equilibrium constant is the same within experimental error when 1.35 mols of mercury, removing about one-third of the sodium, and 5.05 mols of mercury, removing about two-thirds of the sodium, were used. This contradiction between the evidence furnished by the color of the solution as to the amount of sodium present and that furnished by analysis, was further studied.

To test the reversibility of the color change an ether solution of sodium diphenylanisylmethyl was prepared in the usual way and decanted into a two-tube system which was then sealed off. One of these contained saturated amalgam about 1%, and the other connected to it, mercury. The red solution changed to yellow upon pouring into the mercury tube and shaking, and the original color was restored upon pouring back and shaking in the amalgam tube. This was repeated ten times with the same result, even though according to the equilibrium measurements very little sodium would be removed in the mercury tube after the first few times.

It appeared possible that a derivative containing two atoms of sodium was being formed, the red color being due to small amounts of the disodium compound and this second sodium atom being readily removed by amalgams more concentrated than those ordinarily at equilibrium with the monosodium derivative. If so this derivative should be formed completely with 40% amalgam. To test this some of the chloride was first treated in the usual way with 1% amalgam in ether solution and then poured onto 40% sodium amalgam and shaken. No deepening of the color could be noted and after decanting and shaking with mercury in the last tube, the yellow color of the previous runs was noted. Usual analyses gave the same equilibrium constant within experimental error. In addition the ether phase was hydrolyzed with water and the sodium hydroxide formed titrated. The sum of the titrations of ether and mercury phases gave 0.0001247 mole, 0.0001238 mole of chloride having been used, which agrees well within experimental error and shows that the monosodium derivative was formed quantitatively.

It appears possible that a quantity of impurity in amounts too small to affect the analytical results might be present and this form a red sodium addition compound from which the sodium is easily removed by mercury. However, an additional crystallization of the chloride this time from benzene and petroleum ether gave the same red colored solution upon treatment with 1% amalgam.[5]

Tri-*p*-anisylmethyl.—Trianisylcarbinol was made according to the directions of Baeyer and Villiger.[6] After the sulfuric acid addition product was decomposed with water, the product was extracted with ether. A large volume of ether is needed since some of the methane tends to precipitate at this stage as an asbestos-like gummy material. The distilled product was orange-red and fragrant. It was not crystallized before oxidation[1,7] which was followed by conversion to the picrate. This was digested with hot chloroform for half an hour and filtered by suction. It was then shaken in a mechanical shaker with a large amount of dilute alkali. On extraction with ether, desiccation over calcium chloride and evaporation, an orange oil was obtained which solidified on seeding with some of the solid which formed on the lip of the flask. Some of the oily carbinol was dissolved in benzene, calcium chloride added and the solution saturated with hydrogen chloride. The solution became deep red and a red precipitate formed which later turned to a red oil below the benzene. The two liquid phases were decanted from the calcium chloride and boiled down to about 75 cc. On standing for several days some deep red rosets together with some red gum separated slowly. The clear liquid was decanted, an equal volume of absolute ethyl ether added and the solution allowed to stand overnight at 0°. Large white plate-like crystals formed which were dissolved in 30 cc. of benzene. Where the solid came in contact with air it became brick-red. When the operations were carried out in an atmosphere of carbon dioxide no marked coloration occurred. The chloride after recyrstallization was washed with absolute ether several times and dried under reduced pressure over potassium hydroxide. The compound melted at 158°; that previously reported[8] at 154–156°.

Practically no information exists about the free radical. Wieland[9] states that the free radical tri-*p*-anisylmethyl is obtained by the splitting in ligroin of an azo compound, but he gives no description of the free radical. There are no other references to it in the literature. We obtained an orange solution with some orange precipitate upon dissolving the chloride in ether and shaking with mercury. The color disappeared upon admitting air. With a more dilute solution, 0.02 g. of chloride in 100 cc. of ether, shaken with mercury an orange solution formed without a red precipitate.

A sample of the chloride in ether was shaken with saturated amalgam. The solution became orange. After shaking for almost an hour a brown

[5] Another possible explanation, suggested by Dr. W. L. Gilliland, is that sodium diphenylanisylmethyl exists in two tautomeric forms, one red and the other yellow or much lighter, the red existing in small amounts the sodium of which is readily removed by mercury. One would have to postulate in addition that the equilibrium between these two forms is mobile while in contact with amalgam, but not over mercury. In order to shed further light on this peculiar behavior the trianisylmethyl was studied.

[6] Baeyer and Villiger, *Ber.*, **35**, 1197 (1902).

[7] See also Lifschitz and Girbes, *Ber.*, **61**, 1463 (1930).

[8] Ref. 6, p. 3031.

[9] Wieland, *Ber.*, **55**, 1830 (1922).

suspension slowly formed and in several hours the orange color had completely disappeared.

It was thought that possibly the saturated amalgam was too strong a reducing agent and that the use of a very dilute amalgam would enable equilibrium measurements to be made.

0.614×10^{-4} mole of chloride in ether solution was shaken in a single tube carrying a stopcock with an amalgam the mole fraction of sodium in which was 0.743×10^{-4} which is about the mean concentration of the amalgams in equilibrium with diphenylanisylmethyl and its sodium derivative (see Table I). An orange colored solution together with some gray precipitate which may have been entirely sodium chloride was formed. After shaking overnight in the dark the amalgam phase was withdrawn through the stopcock and titrated. Water was then admitted to hydrolyze the ether phase and precipitate, and the mixture titrated. The orange colored solution did not change color upon adding water but was instantly decolorized by air.

To summarize the titration results

0.10×10^{-4}	mole of sodium in ether phase + ppt.
0.81	mole of sodium in amalgam after shaking
0.61	mole of sodium equivalent to Cl in original chloride
1.52	mole of sodium sum
1.46	mole of sodium in original amalgam

Considering that the end-point was not very good in titrating the ether and precipitate, these two figures check quite well.

These figures indicate that the tri-*p*-anisylchloromethane reacts quantitatively with this dilute amalgam to form the free radical but that no appreciable amount of sodium adds to the free radical to form the sodium derivative. We prepared an amalgam the mole fraction of sodium in which was 6.04×10^{-4}, about eight times as strong as the preceding one. This was done in order to force more sodium into the ether phase. In this experiment an apparatus with two tubes, similar to those used in the equilibrium measurements was used, except that the first tube also had a stopcock. 0.878×10^{-4} mole of chloride was shaken in the first tube with the amalgam. The solution turned orange and remained so upon shaking overnight in the dark. The solution was decanted and filtered into the second tube and mercury added and this shaken overnight in the dark. The orange color did not lighten after shaking with mercury, or upon admitting water, but was decolorized in air. Both phases in the second tube and the amalgam and precipitate in the first tube were hydrolyzed and titrated with the following results. The amount of sodium in the original amalgam was 3.07×10^{-4} gram atom. The amount remaining at the conclusion of the experiment was 1.93×10^{-4} gram atom. About 0.08×10^{-4} gram atom was found in the precipitate formed in the first tube. 0.88

$\times 10^{-4}$ gram atom is the amount which should be required to convert the chloride into the free radical. These amounts add up to give 2.89×10^{-4}, nearly the amount of sodium introduced in the original amalgam. This agrees with the fact that no sodium was removed by the mercury and none found in the ether phase. One may conclude, therefore, that tri-*p*-anisylmethyl may be prepared from the chloride by treatment with either mercury or an amalgam whose mole fraction of sodium is from zero to 0.7×10^{-4}. Since no sodium addition compound has been prepared, it is not possible to give a value for the free energy change for the reaction. It may be somewhat less negative than for the compounds heretofore studied.

Pentaphenylcyclopentadienyl.—This free radical has been prepared by Ziegler and Schnell,[10] who found it to be completely dissociated by freezing-point measurements.

In the preparation of methylene-bis-desoxybenzoin, it was found important that desoxybenzoin should be pure, and that alkali should not be added until the formalin had been well mixed with the solution. It is desirable to cool the solution to 0° during the slow addition of alkali. Under these conditions crystals began to appear almost at once and there was no oily phase. When the reaction was carried out at room temperature, however, and the alkali added rapidly, the gummy material described by Ziegler and Schnell was obtained. Heat is liberated when the ketone is added to the final Grignard solution at the boiling point of ether, and a considerable amount of tarry by-products appeared. But when the Grignard solution was cooled to 0° and the ketone added slowly, a good yield of carbinol was obtained. This was crystallized twice from acetic acid and converted into the chloride, which melted at 170°. The value previously reported is 167°.

A sample of the chloride in ether solution was treated with 1% amalgam in the usual system. A purple colored solution was formed at first. This is the color of the free radical in benzene described by Ziegler and was also obtained by shaking an ether solution of the chloride with mercury. After shaking with the amalgam a short while, a dirty green precipitate was formed and the purple color disappeared. The ether phase remaining contained no hydrolyzable sodium.

It was thought that possibly the sodium derivative was formed but was insoluble in ether and might be soluble in benzene. The experiment was repeated using very dry benzene in place of the ether. The same phenomena occurred again although the purple color persisted longer than when in ether solution. In order to learn whether or not a more dilute amalgam would give the free radical as in the case of tri-*p*-anisylmethyl another sample of the chloride in ether solution was treated with a very dilute amalgam the mole fraction of sodium in which was 0.743×10^{-4}. Here again the same phenomena were noted, the purple solution forming at first and then a green precipitate.

The analysis of the amalgam indicated that not more than one and one-half equivalents of sodium had reacted with the chloride, one equivalent

[10] Ziegler and Schnell, *Ann.*, **445**, 274 (1925).

of this being required to form the free radical. Evidently the presence of sodium amalgam catalyzes the decomposition of the free radical.

Oxygen and Nitrogen Free Radicals.—We are indebted to Professor L. F. Fieser for the 9-chloro-10-phenanthrol used in these experiments. This material had been prepared by the method of Schmidt and Lumpp and melted at 122°. The previously recorded value is 121°.[11]

Goldschmidt and Steigerwald[12] prepared the free radical by oxidation with lead dioxide and found it to exist in the dissociated form in several solvents.

Upon treating the phenanthrol with sodium amalgam a reaction took place which should give the same compound as would be obtained by addition to the free radical. The solution remained colorless and on shaking with mercury no sodium was removed. Ninety per cent. of the calculated amount of sodium was found in the ether solution by titration. The original phenanthrol was recovered after the titration, and identified by a mixed melting point.

This experiment clearly indicates that an oxygen-free radical unites with sodium to form a compound which is much more stable than the corresponding carbon compound. One can place the free energy change for this reaction qualitatively by saying that it is more negative than in the case of carbon by at least 5 kg. cal.

One might expect from the foregoing experiment on the oxygen-free radical that a nitrogen-free radical would show a similar behavior but would hold to the sodium less firmly. The choice of largely dissociated nitrogen free radicals is, however, very limited. α,α-Diphenyl-β-trinitrophenylhydrazyl was synthesized by the method of Goldschmidt and Renn.[13] However, treatment of the hydrazine with the sodium amalgam resulted in side reactions which prevented further study with this compound. Doubtless the nitro groups are responsible for the various reactions observed.

We are indebted to the Milton Fund of Harvard University for financial support in this investigation.

Summary

1. ΔF for the addition of sodium to diphenylanisylmethyl is the same as for the addition of sodium to triphenylmethyl.

2. ΔF for the addition of sodium to the oxygen free radical, 9-chloro-10-phenanthroxyl, is more negative than for carbon free radicals by at least 5 kg. cal.

3. The following compounds will give no sodium addition compound when treated with a one per cent. sodium amalgam, presumably due to the

[11] Schmidt and Lumpp, *Ber.*, **41,** 4215 (1908).

[12] Goldschmidt and Steigerwald, *Ann.*, **438,** 202 (1924).

[13] Goldschmidt and Renn, *Ber.*, **55,** 636 (1922).

presence of side reactions: pentaphenylcyclopentadienyl, tri-*p*-anisylmethyl and the nitrogen free radical α,α-diphenyl-β-trinitrophenylhydrazyl.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

THE HEAT CAPACITY OF SELENIUM FROM 100 TO 300°A.[1]

BY THOS. DE VRIES AND L. FRANCIS DOBRY

RECEIVED MAY 16, 1932 PUBLISHED AUGUST 5, 1932

Previous work on the heat capacity of metallic selenium has been of a rather uncertain nature. None of the experimenters has stated the method of purification so as to have selenium free from tellurium, nor have they shown that their specimens were the metal and not some other form of selenium.

Some of the earliest work was done by Regnault.[2] He obtained the value 6.63 calories per mole at 98° and 5.93 at 20 to 98°. Bettendorf and Wüllner[3] found 6.65 from 25 to 60°. Dewar[4] gave the value 2.86 between liquid nitrogen and liquid hydrogen temperatures. In our investigation the selenium was carefully purified and annealed to the metallic form. The Nernst method was used to find the heat capacity.

Purification and Preparation of the Sample

A Mallinckrodt grade of selenium was dissolved in concentrated nitric acid. The selenium dioxide was then dissolved in dilute hydrochloric acid. The insoluble material was filtered out and the selenium precipitated with sulfur dioxide. The selenium came down in the red form and turned black upon drying. This was repeated twice. For the complete removal of tellurium, the method of Lenher and Kao[5] was used, in which hydroxylamine hydrochloride was used as the reducing agent. This purification was also repeated twice. This gave a black form of selenium. The wet selenium was washed with alcohol and vacuum dried at room temperature. This amorphous selenium was then placed in a Pyrex glass tube, connected to a vacuum pump and heated. Large volumes of gas came off, and finally a tarry mass was formed. This was allowed to cool to a shiny black, brittle solid in an atmosphere of nitrogen.

The selenium was transferred to a soft glass cylinder and melted. In this was inserted two Pyrex thermocouple wells, and a spiral heating coil of No. 30 nichrome wire. (Approximate resistance was 11 ohms.) The entire assembly was then heated in an oil-bath to 210–215°, where it was kept for several hours. It was then allowed to cool slowly in a Dewar flask filled with oil of about 225°. At the end of eight hours the temperature of the oil was still about 50°, so it was assumed that only the metallic

[1] This article is an abstract of the thesis presented by L. F. Dobry to the Faculty of the Graduate School of Purdue University in partial fulfilment of the requirements for the degree of Master of Science.

[2] Regnault, *Ann. chim. phys.*, [2] **73**, 51 (1840); [3] **46**, 281 (1856).

[3] Bettendorf and Wüllner, *Pogg. Ann.*, **133**, 293 (1868).

[4] Dewar, *Proc. Roy. Soc.* (*London*), **89**, 158 (1913).

[5] Lenher and Kao, THIS JOURNAL, **47**, 2454 (1925).

form of selenium was present. This procedure, and the assumption that only the selenium metal was present after cooling, is substantiated by Saunders and Mellor in their publications.[6] The soft glass was then broken away, leaving a selenium slug of 32 mm. outside diameter by 60 mm. long and weighing 189.14 g. No. 30 copper wires were silver soldered to the nichrome heating element, and copper–constantan thermocouples were fixed in the wells with paraffin.

The selenium slug was suspended by fine silk thread inside a copper jacket, 4.8 cm. in diameter and 13.2 cm. long, weighing 1260 g. The thermocouple and electric heater wires from the selenium were taken out through a copper tube fastened to the lid. The entire length of the jacket was wound with No. 30 D. S. C. manganin wire, which was firmly cemented on with bakelite varnish. To the inside of the jacket was fastened a copper–constantan thermocouple. These circuits were used to adjust the temperature of the jacket equal to that of the selenium sample.

The thermostat consisted of a long Pyrex glass cylinder, 6.3 cm. in diameter by 46 cm. deep. Into the upper end was ground a 250-cc. flask which served as a stopper, and from its neck was suspended the jacket containing the selenium. The joint was sealed with de Khotinsky cement. To the sides, 10 cm. from the top, were sealed three tubes. One was connected to a mercury vapor pump, another served as an outlet for the thermocouples and heating element wires. The third tube, filled with 2.54 cm. of dibutyl phthalate, served to contain the cold junctions of the thermocouples. This cylinder, or thermostat proper, was placed in a Dewar flask, 14 cm. in diameter and 32 cm. deep, so that it could be surrounded by a suitable cooling bath. The liquid level of the bath was at least 10 cm. higher than the upper end of the copper jacket.

Electrical Standards and Experimental Technique.—A carefully prepared manganin resistance, which was frequently calibrated against a standard resistance furnished by Leeds and Northrup, was used in series with the nichrome heating coil of the selenium sample. This prepared resistance had a value of 1.0751 ohms. If E_1 and E_2 represent the volts across the nichrome heating element in the selenium, and across the standard resistance, the number of calories produced per second in the selenium is given by

$$\frac{E_1 \times E_2}{1.0751 \times 4.181}$$

In order that the voltage across the heating coil could be read on the type K potentiometer, a resistance of 1100 ohms was placed in parallel with the heating coil, and a tap taken off at about the 100 ohm value. The ratio of the tapped resistance to the entire resistance was found to be 1 : 100.84.

The thermocouples were calibrated against a platinum resistance thermometer, recently calibrated by the Bureau of Standards. The e. m. f. values for copper–constantan thermocouples given by Southard and Andrews[7] were used as a standard. The following were the observed corrections for the two-couple thermel used in the sample.

[6] A. P. Saunders, *J. Phys. Chem.*, **4**, 423 (1904); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, p. 705.

[7] Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

TABLE I

THERMOCOUPLE CORRECTIONS

Temperature of bath, °A.	84.60	151.43	209.06
Observed e. m. f., mv.	10523	7734	4469
Calculated e. m. f., mv.	10623	7798	4497
Deviation, mv.	+100	+64	+28

These deviations lie on a smooth curve fitted by the equation

$$\Delta \text{ mv.} = 3.51\ (e/1000) + 0.616\ (e/1000)^2$$

As thermostatic liquids in the large Pyrex Dewar flask, there were used liquid air, carbon dioxide snow and ether, carbon dioxide snow and chloroform or ice and water, depending on what temperature was desired. After a constant temperature was obtained in the slug, the apparatus was evacuated. A record of the temperature of the selenium was made until a constant change was observed. The heating current was then turned on for ten minutes, the time being measured with a stop watch to one-fifth of a second. While the current was on, the e. m. f. across the tapped resistance and the standard resistance were taken alternately every minute. At the end of ten minutes, the current was shut off, and the e. m. f. across the two-couple thermel was again taken, until a constant change of temperature was again observed. The method of Jaeger and Steinwehr[8] was used to calculate the correction for heat lost and gained during the time that the selenium was heated and the temperature became constant. The correction amounted to about ten per cent. of the total temperature rise. These

TABLE II

DATA FOR THE HEAT CAPACITY OF SELENIUM

Temp., T, °A.	E. m. f. change	Temp. rise, °C.	E. m. f. across tapped resis., mv.	E. m. f. across std. res., mv.	C_p, cal./mole obs.	C_p, cal./mole calcd.
98.3	10242–9934	8.28	29415	295570	5.92	6.03
100.8	10146–9847	7.91	29399	295490	6.19	6.08
103.6	10038–9736	7.84	29415	294960	6.24	6.11
112.5	9696–9379	7.79	28973	291040	6.10	6.24
141.1	8447–8095	7.21	29065	290510	6.60	6.50
141.5	8427–8078	7.31	29081	290720	6.52	6.52
153.8	7837–7463	7.38	29153	290720	6.46	6.58
207.9	4792–4327	7.40	29904	295010	6.72	6.72
276.9	539–48	6.42	28187	275580	6.82	7.01
277.1	572–32	7.05	30154	294130	7.09	7.02
278.3	666–126	7.03	30088	293890	7.11	7.02

Ratio factor of tapped resistance, 100.837. Standard resistance, 1.07508 ohms. Weight of selenium sample, 189.14 g. = 2.388 moles.

[8] Oswald-Luther, "Physiko-chemische Messungen," 4th ed., pp. 365–371.

corrections are included in the values of column two of Table II, in which the changes in observed microvolts are tabulated. The change in the thermocouple correction with change in temperature was also considered in calculating the temperatures, tabulated in column three of Table II. The values lie on a reasonably smooth curve, fitted by the equation

$$C_p = 2.69 + 0.0560\ T - 2.66 \times 10^{-4}\ T^2 + 4.35 \times 10^{-7}\ T^3$$

The values in the last column of Table II have been calculated by the use of the above equation.

Summary

1. The heat capacity of metallic selenium was determined by the Nernst method. The selenium was carefully purified by the Lenher and Kao method.

2. The experimental values for the temperature range from 100 to 300°A. lie between 6.08 and 7.25. Values for this range have not been reported previously. The value calculated for 300°A. is approximately ten per cent. larger than that reported by Bettendorf and Wüllner.

W. LAFAYETTE, INDIANA

NOTES

The Standardization of Weights

BY FRED C. EATON

The method of Richards[1] for calibrating a set of weights has one particularly attractive feature, the procedure used in calculating the corrections from the system of observation equations. The discussion which follows will show that this procedure gives values which are exactly the same as the values defined by the system of equations. In other words, they are identical with the values to be found by substituting in algebraic formulas like those of Kohlrausch.[2]

The Reasoning of Richards.—A study of what Richards has written will explain why some do not appreciate just how accurate the calculation is. His preliminary values are *consistent* by reason of two assumptions. First, there is the assumption that the first centigram weight, called the standard of comparison, has the mass of 0.01 g. Second, it is implicitly assumed that the small differences between the masses of the various combinations of weights have been correctly measured by the rider in terms of grams. These consistent values are then translated into other terms by a method depending upon the properties of small numbers in presence

[1] T. W. Richards, THIS JOURNAL, **22**, 144 (1900); *Z. physik. Chem.*, **33**, 605 (1900).

[2] F. Kohlrausch, "Lehrbuch der praktischen Physik," 11th edition, p. 62.

of large ones.[3] This reasoning may well confuse those who study it carefully. Semon,[4] for example, was guided by it in making his analysis.

A Different Interpretation.—That procedure of Richards will now be explained in a different way. Let the symbol (A) denote the actual number of grams in the mass of the weight whose face value is A grams. Moreover, let (0.01) denote the mass of the first centigram weight. Then, if $[A]$ and [0.01] are the corrections for these weights, the relation between their masses is expressed by the equation

$$(A) = [A] + 100\,A\,\{(0.01) - [0.01]\}$$

The first step in calculating the corrections is to find from the equations a preliminary value for each weight. In doing this we shall make no assumption regarding the mass of the first centigram weight. The preliminary values in Table I are *defined* by assigning to (0.01) the value 0.[5] Hence, it follows immediately from the preceding equation that

$$\text{Preliminary value of } (A) = [A] - 100\,A\,[0.01]$$

TABLE I

$(A) = A + [A]$ $(0.01) = 0.01 + [0.01]$ Standard: (100) = 100.00158 g.

(A)	Observation equations	Grams	Preliminary values $[A] - 100\,A\,[0.01]$	Aliquot parts $100\,A\,[0.01]$	Corrections $[A]$, milligrams
(0.01)	...	.....	0.00000	+0.00007	+0.07
(0.01′)	= (0.01)	−0.00006	− .00006	+ .00007	+ .01
(0.01″)	= (0.01)	− .00009	− .00009	+ .00007	− .02
(0.02)	= (0.01) + (0.01′)	− .00004	− .00010	+ .00014	+ .04
(0.05)	= Σ(0.05)[a]	− .00013	− .00038	+ .00035	− .03
(0.1)	= Σ(0.1)	− .00013	− .00076	+ .00070	− .06
(0.1′)	= (0.1)	+ .00006	− .00070	+ .00070	.00
(0.2)	= (0.1) + (0.1′)	+ .00002	− .00144	+ .00141	− .03
(0.5)	= Σ(0.5)	+ .00005	− .00348	+ .00352	+ .04
(1)	= Σ(1)	− .00008	− .00709	+ .00703	− .06
(1′)	= (1)	+ .00013	− .00696	+ .00703	+ .07
(1″)	= (1)	+ .00003	− .00706	+ .00703	− .03
(2)	= (1) + (1′)	+ .00002	− .01403	+ .01407	+ .04
(5)	= Σ(5)	+ .00004	− .03510	+ .03517	+ .07
(10)	= Σ(10)	− .00014	− .07038	+ .07035	− .03
(10′)	= (10)	+ .00030	− .07008	+ .07035	+ .27
(20)	= (10) + (10′)	+ .00043	− .14003	+ .14069	+ .66
(50)	= Σ(50)	+ .00024	− .35049	+ .35173	+1.24
(100)	= Σ(100)	− .00067	− .70189	+ .70347	+1.58

[a] The meaning of this notation is shown by the following example: Σ(5) = (2) + (1″) + (1′) + (1).

[3] When α and β are quite small in comparison with N, then $N\,(N + \alpha)/(N + \beta) \simeq N + \alpha - \beta$.

[4] W. L. Semon, *J. Chem. Ed.*, **2**, 132 (1925).

[5] As we are giving a definition, this value may be chosen arbitrarily. The preliminary values of Richards would result from setting (0.01) = 0.01000.

This equation easily explains the rest of the procedure. Let the last term *define* what we mean by the aliquot part for (A). Then it is self-evident that, when the aliquot part for one weight is known, the aliquot parts for all the others can be found. Theoretically, if we know the correction for *any* one weight, we can quickly calculate the corrections for all the others. In practical work, however, the face value of the standard should not be less than that of the largest weight in the set.

This explanation of the procedure of Richards makes no assumption and requires the use of no approximation. Consequently that procedure gives values which are precisely the same as those defined by the system of equations, and the accuracy of those values depends solely on the errors made in measuring the small differences between the masses of the various combinations of weights.

Another convenient method of arranging the computation is shown in Table II. This arrangement has the advantage of using smaller numbers. A few additional remarks will make the procedure clear. In dealing with the first group we know the mass of the weight (100) and we define the preliminary values by assigning to (10) the value 0. When we come to the second group, we know the mass of the weight (10) and we define the preliminary values by assigning to (1) the value 0.

TABLE II

Observation equations		Grams	Preliminary values	Aliquot parts	Corrections, milligrams
(10)	....	.....	0.00000	−0.00003	−0.03
(10′)	= (10)	+0.00030	+ .00030	− .00003	+ .27
Σ(10)	= (10)	+ .00014	+ .00014	− .00003	+ .11
(20)	= (10) + (10′)	+ .00043	+ .00073	− .00007	+ .66
(50)	= Σ(50)	+ .00024	+ .00141	− .00017	+1.24
(100)	= Σ(100)	− .00067	+ .00191	− .00033	+1.58
(1)	...	.....	0.00000	−0.00006	−0.06
(1′)	= (1)	+0.00013	+ .00013	− .00006	+ .07
(1″)	= (1)	+ .00003	+ .00003	− .00006	− .03
(2)	= (1) + (1′)	+ .00002	+ .00015	− .00011	+ .04
(5)	= Σ(5)	+ .00004	+ .00035	− .00028	+ .07
(10)	= Σ(10)	− .00014	+ .00052	− .00055	− .03[a]

[a] This value has been taken from the corrections for the preceding group of weights.

Summary.—The procedure of Richards for calculating corrections from the system of observation equations has been discussed. It has been shown that this procedure gives values which are identical with those to be found by substituting in algebraic formulas like those of Kohlrausch.

EASTON, PENNSYLVANIA

RECEIVED OCTOBER 27, 1931
PUBLISHED AUGUST 5, 1932

Alkaline Persulfate as an Analytical Reagent

By William M. Dehn and Donald A. Ballard

Though persulfate in acid[1] or neutral solutions[2] has frequently been applied as a qualitative reagent, its use in alkaline[3] solution has been limited to the precipitation of cobaltic oxide. Using potassium persulfate in potassium hydroxide solution, instead of ammonium persulfate in sodium hydroxide solution as used by Pozzi-Escot, a more complete precipitation of Co_2O_3 can be made (1:1,000,000).

Comparable precipitations of black Ni_2O_3 can be made from nickelous solutions by treatment with alkaline persulfate. In the absence of cobalt, it is a characteristic test for nickel, since its black will cover up the colors of other metallic hydroxides. Also in the presence of metals whose hydroxides are soluble in fixed alkalies, it can give a separation of either nickel or cobalt or both of these metals. Conversely nickel or cobalt is a qualitative test for persulfate.

Cyanides.—Alkaline persulfate oxidized cyanides, ferricyanides, ferrocyanides, nitroprussides and thioazanates to cyanic acid, as indicated by the following test. To any one of these, add the reagent and heat to boiling. Acidify with hydrochloric acid and again make alkaline. Moist red litmus paper on the convex side of a watch glass covering the beaker turns blue, owing to the liberation of ammonia. Without persulfate, the litmus paper remains unaffected.

Thiosulfate, but not sulfite, or arsenite, is oxidized by the reagent. Sodium peroxide liberates oxygen. These and other reactions will be studied.

[1] Caro, *Z. angew. Chem.*, 845 (1898); Marshall, *Chem. News*, **83**, 76 (1901).

[2] Merk, *Pharm.-Ztg.*, 1022 (1905); Pozzi-Escot, *Compt. rend.*, 435, 1334 (1907).

[3] Pozzi-Escot, *Ann. chim. anal. chim. appl.*, **13**, 390 (1908); **14**, 207 (1909); Bollenbach, *Z. anal. Chem.*, **47**, 690 (1908).

Chemical Laboratory
University of Washington
Seattle, Washington

Received March 14, 1932
Published August 5, 1932

A Lubricant Insoluble in Organic Solvents

By C. C. Meloche and W. G. Fredrick[1]

In working with organic solvents it is occasionally necessary to lubricate a stopcock or ground-glass joint in such a manner as to maintain a vacuum or a gas-tight seal and at the same time withstand the solvent action of the liquid. Under such conditions lubricants containing petroleum grease or rubber are as a rule useless on account of their solubility in the solvent and inorganic lubricants are often unsuitable due to separation of a constituent, reaction with the solvent, solubility or freezing.

[1] Mallinckrodt Fellow in Chemistry, University of Michigan, 1930–1932.

A solution of dextrin in glycerin is occasionally recommended[2] as a lubricant under the special conditions mentioned. The insolubility of this material in many organic solvents, as well as the high viscosity and slightly adhesive quality, renders this mixture suitable where a gas-tight seal is needed but where the frequent turning of a stopcock is unnecessary. The writers have found that the addition of mannitol in proper amount imparts the correct lubricating quality and renders this lubricant practically indispensable in certain types of work. For general use the lubricant may be prepared as follows.

Mix thoroughly 25 g. of anhydrous glycerin, 7 g. of dextrin and 3.5 g. of chemically pure *d*-mannitol until a thick paste is obtained. Heat carefully with constant stirring until the solid material is dissolved and the solution just begins to boil. A small amount of water is lost. Cool the clear, colorless or sometimes slightly turbid liquid with occasional stirring to room temperature. The liquid becomes highly viscous and finally acquires a lustrous white or opalescent appearance due evidently to the separation of part of the mannitol in a finely divided state. This preparation has excellent lubricating qualities as well as the body and adhesiveness suitable for most purposes. To increase the viscosity add more dextrin. To increase the fluidity add more glycerin. To impart the physical property of a greasy paste add a little more mannitol. Chemically pure *d*-mannitol is recommended, since commercial mannitol will not always yield the desired result. This lubricant is best stored in an ointment jar or kept in a desiccator, but exposure to laboratory air is not harmful.

The action of a number of solvents on this lubricant was tested as follows. The stopper of a small Erlenmeyer flask was lubricated so as to give a thin uniform film on both ground glass surfaces when the stopper was inserted. The stopper was removed, both lubricated surfaces were drenched with the solvent to be tested, and the excess of the solvent shaken or blown off. The stopper was then replaced in the flask and rotated to test the lubricating action. After repeating the operations of drenching and testing a number of times alternately the relative effects of the various solvents could be easily observed.

Tested in the manner described, the following solvents had no detectable effect, or at most a very slight and negligible effect: acetic anhydride, acetophenone, benzaldehyde, benzene, bromobenzene, carbon bisulfide, carbon tetrachloride, chlorobenzene, tetrachloroethane, cyclohexane, ethyl acetate, ethyl acetoacetate, ethyl bromide, ethyl carbonate, ethylene dichloride, methyl acetate, methylaniline, nitrobenzene, nitromethane, petroleum ether, diphenyl ether, toluene, *o*-toluidine, turpentine, *o*-xylene.

The following solvents had a slight effect, not, however, sufficient to prevent the use of the lubricant provided the latter is renewed when

[2] Iredale, *Phil. Mag.*, **45**, 1097 (1923).

necessary: acetaldehyde, acetone, acetyl chloride, amyl acetate, amyl nitrate, benzoyl chloride, *n*-butyl ether, diethyl ether, methylene chloride.

The solvent or disintegrating action of the following was sufficient to prevent or greatly hinder the use of the lubricant: aniline, acetic acid, tertiary amyl alcohol, benzyl alcohol, *n*-butyl alcohol, tertiary butyl alcohol, ethyl alcohol, methyl alcohol, diethylamine, ethylene chlorohydrin, ethylene glycol, formic acid, propionic acid, pyridine, quinoline, water and solvents containing water. In general, therefore, water, alcohols, aliphatic acids and to a lesser extent certain amines and nitrogen containing heterocyclic compounds prevent the use of the lubricant.

Before lubricating a stopcock with this preparation, petroleum and rubber grease should be entirely removed by means of benzene or acetone and the stopcock should be thoroughly dried. After applying a thin film of the lubricant, a stopcock will remain gas tight even when frequently turned in the presence of solvents of the first group mentioned above. With a liquid-air trap in the line to remove any water vapor evolved, a stopcock lubricated as described will hold a good vacuum. In gas analytical operations where the presence of petroleum grease was thought to cause error by absorbing constituents such as ether vapor, the glycerin–dextrin–mannitol lubricant has been used with success. Water dissolves the lubricant readily and may therefore be used to remove it when desired.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

RECEIVED APRIL 27, 1932
PUBLISHED AUGUST 5, 1932

The Probable Non-Existence of Normal Tribasic Aluminum Soaps Such as Aluminum Tripalmitate

BY JAMES W. MCBAIN AND WINIFRED L. MCCLATCHIE

Aluminum soaps are articles of commerce used in several industries; they are even listed in most catalogs of pure reagents, and they have frequently been employed in scientific work.[1] Nevertheless, after repeated purchases and attempts to prepare aluminum tripalmitate and other tribasic aluminum soaps, we have come to the conclusion that the product is a mechanical mixture from which an appreciable proportion of free fatty acid is at once dissolved by ether, leaving behind a monobasic or at most a dibasic soap such as a dipalmitate, even when prepared and extracted in the complete absence of moisture. For example, Kahlbaum's aluminum tripalmitate yielded 50% of its fatty acid content to ether dried over sodium. A sample of aluminum palmitate obtained from Eimer and Amend contained only one equivalent of fatty acid to three equivalents of aluminum.

Aluminum soaps are usually prepared from aqueous solution by pre-

[1] For example, in emulsions of water with other solvents, in studies of swelling, etc.

cipitating a soluble soap with aluminum salt. The precipitate is then taken to be the tribasic aluminum soap. Consideration of the elementary theory of aqueous solutions (compare, for example, aluminum sulfide) would lead one to expect a doubtful or negative result on account of the extensive hydrolysis of a salt of a weak fatty acid with a base at once so weak and insoluble as aluminum hydroxide.

Preparations of Oleates, Stearates, and Palmitates from Aqueous Solutions.—When aluminum sulfate solution was added in excess to an aqueous solution of a sodium or potassium soap, the *P*H of the soap solution changed during precipitation from about 8.5 to about 4.5. The precipitates were washed with water, alcohol and ether or with acetone, and aluminum was determined by ignition as Al_2O_3. They contained from 5.5 to 6.7% aluminum for palmitates and from 5.0 to 6.2% for stearates and oleates. This indicates a gross composition slightly nearer to dibasic rather than monobasic soap, which was confirmed by a determination of fatty acid present. Preparations made when the *P*H was kept equal to 8.5 with sodium bicarbonate gave similar results. With *P*H between 3 and 4.5 the product contained little more palmitic acid than corresponded to monopalmitate.

Preparation of Palmitates in Non-Aqueous Media.—Preparations made in 95% alcohol and in absolute methyl and ethyl alcohols gave results no nearer the tripalmitate. Diamyl ether, a good solvent for aluminum soap, was used with palmitic acid and freshly prepared aluminum hydroxide washed with alcohol and ether. The soap from this solution was no better. Similar procedures with chloroform left as much as 14% of aluminum in the soap even when the solution had become clear.

Finally, we turned to the reaction between aluminum ethoxide and palmitic acid and benzene which had been dried over sodium. Of 2.6 g. of Kahlbaum's ethoxide, 2.0 g. dissolved on refluxing with benzene. When the theoretical amount of Kahlbaum's best palmitic acid was added, the resulting solution was clear and fluid, but after evaporation to dryness a large amount of fatty acid or fatty anhydride was extracted at 40° by dry ether, yielding palmitic acid 92.2 and 93.5% and aluminum 5.10 and 5.15%. This corresponds closely to an anhydride or ethoxide of aluminum dipalmitate (there was no water present at any time for formation of $AlPal._2OH$).

Further experiments in the same direction have been made in the Department of Chemistry, University of Nevada, Reno, by S. Allan Lough and E. L. J. Randall. The Kahlbaum palmitic acid used was found to be 99.9% pure as determined by titration with standard alkali. The ethoxide by ignition indicated a content of 45.28% although only 40% was extracted with benzene, leaving the alumina behind. Another sample of benzene extract contained 88% of material removed from the

crude ethoxide after filtering through surgical absorbent cotton. After reaction with more than the theoretical amount of palmitic acid and extracting the dried (at 45°) product with ether, the aluminum content was 4.8% as compared with the 5.1% already quoted. In a final experiment with dried benzene which had dissolved 77% of the crude ethoxide the product was dried in four portions at 25, 45, 55 and 75°. The crude material contained between 2.85 and 3.00% of aluminum and after hydrolysis with sulfuric acid yielded fatty acid determined by titration in alcoholic potash corresponding to from 78.96 to 94.84% of palmitic acid. These four products after extraction with sodium-dried ether contained, respectively, 5.38 and 4.43, 5.36 and 5.34, 5.29 and 5.20, 5.24 and 5.33% of aluminum, whereas aluminum tripalmitate would contain only 3.400% of aluminum. These results again indicate that not more than the dibasic palmitate is attained even under these unusually favorable conditions.

Our conclusion is that aluminum soaps are commonly a mixture of uncombined free fatty acid with either a monobasic or a mixture of mono- and dibasic soaps. Normal tribasic aluminum soaps have never been prepared even in completely anhydrous media.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED MAY 23, 1932
PUBLISHED AUGUST 5, 1932

[CONTRIBUTION FROM THE MEDICAL SCHOOL, UNIVERSITY OF OTAGO, NEW ZEALAND]

THE DETERMINATION OF IODINE IN BUTTERFAT

BY H. A. A. AITKEN

RECEIVED DECEMBER 12, 1931 PUBLISHED AUGUST 5, 1932

The estimation of iodine in carbonaceous materials such as oil or butter is generally regarded as the most difficult of all estimations of minute amounts of iodine in natural products. The most recent method that has been described is that of McClendon, Remington, von Kolnitz and Rufe,[1] in which melted butter (as much as 500 g. in one sample) was sprayed from an atomizer into a silica tube and burnt with a current of oxygen in the presence of a catalyst. This process obviates the difficulty inherent in the much simpler method of combustion with alkali, namely, that the low iodine content of the material necessitates so large a sample being taken for analysis that the use of an excess of potash is out of the question. This leads to loss of iodine, and in addition there is a pronounced tendency for the products of saponification of the butter to froth up during combustion in an uncontrollable fashion.

However, in the micro-titration method devised by the author for the

[1] J. F. McClendon, Roe E. Remington, Harry von Kolnitz and Redding Rufe, THIS JOURNAL, 52, 541 (1930).

analysis of blood for iodine,[2] as little as 0.4 microgram of iodine in the sample suffices if the worker is content with a possible error of not more than 5%. When this method is applied to butter or butterfat (average iodine content about 20 microgram/kg.), a comparatively small sample of 25 g. will provide sufficient material for an analysis.

As a result it is possible to carry out a gentle combustion in the presence of an amount of caustic potash far in excess of that required to saponify the butter. Under these conditions, indeed, the process except in its final stages is better described as an alkali-fusion, the evolution of hydrocarbons from the melt taking place at a relatively low temperature. The iodide formed can be extracted readily and quantitatively from the resulting potassium carbonate and estimated immediately by titration. The method is a much more rapid one than the silica-tube method and probably gives more accurate results.

The procedure in actual practice is as follows: 25 g. of butter (or butterfat) is placed in a 20-cm. nickel basin and 20 cc. of 50% caustic potash is added, followed by 80 cc. of alcohol. All reagents and vessels used must be iodine-free. The butter is saponified by heating for an hour on the water-bath, and the contents of the basin are then evaporated gently to dryness on the sand-bath. The dry residue is now ignited below red heat over a gas-ring. The arrangement used to avoid overheating is shown in Fig. 1. The basin is set in a shallow iron dish about 15 cm. in diameter and 3.8 cm. deep, the depth being such that an air space intervenes between the bottom of the basin and the iron dish. This eliminates the possibility of local overheating. A trial is made with the basin empty and shaded from direct light to determine how strong a flame can be used without bringing the bottom of the basin to a glow. At this temperature the contents of the basin are found to form a melt from which hydrocarbons are evolved over a period of about three hours, the volume of the melt at the same time steadily diminishing. The process is accelerated by occasionally stirring with a nickel spatula set in a wooden handle, and distributing the material over the heated surface of the basin.

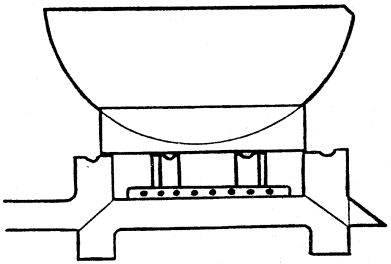


Fig. 1.

When evolution of gases has ceased, combustion is continued for a further half hour or more until a gray layer of potassium carbonate remains in the basin. The basin is cooled and the layer of salt washed down with a small amount of water, evaporated to dryness, and again ignited for half an hour. The residue is now taken up with about 150 cc. of water and filtered hot with gentle suction using a 10-cm. Büchner funnel and a 250-cc. filter flask. A fast pipet (about 50-cc.) can be used to transfer the liquid from the basin to the filter; the pipet is rinsed into the empty basin and this liquid is used to wash the precipitate. The filtrate and washings, which should be almost colorless, are now transferred to a clean basin and evaporated to dryness. The residue is ignited as before for a further quarter of an hour and allowed to cool.

Just sufficient half-saturated potassium carbonate solution (about 8 cc.) is now added to produce a smooth paste when rubbed into the residue by means of two stout

[2] H. A. A. Aitken, *Biochem. J.*, **24**, 1456 (1930).

glass rods with flattened ends. Formation of the paste may be assisted by the addition of a few cc. of 90% alcohol. About 25 cc. of 95% alcohol is added and stirred thoroughly into the paste. The extract is decanted into a 100-cc. nickel crucible with the aid of a thin glass rod, the lip of the basin being smeared with vaseline. The extraction is repeated two or three times, a total volume of about 75 cc. of alcohol being employed. If the paste has been made too thin it is an advantage to use absolute alcohol for the extraction; if it becomes too stiff, 90% alcohol is used.

The alcoholic extract with the addition of a little water is gently evaporated to dryness on the sand-bath. The residue of salts is rinsed down with a thin stream of water from a wash bottle, only a few cc. being employed, and the resulting solution is decanted into a 25-cc. nickel crucible. The process is repeated two or three times, a total of about 18 cc. of water being used. The contents of the small crucible after addition of about 10 drops of saturated potassium carbonate are evaporated carefully to dryness on the sand-bath and ignited for about five minutes by placing the crucible in a slightly larger one containing a few chips of pipe-clay to prevent actual contact and heating the outer crucible in a large non-luminous flame.

The residue is carefully moistened with a few drops of saturated potassium carbonate solution so as to form a paste as before when rubbed with two small glass rods. The alcoholic extraction is then carried out, this time with successive small amounts of about half a cc. of alcohol. The extracts are decanted into a titration tube, a particle of pumice is dropped in to initiate the boiling, the tube is suitably supported on the sand-bath and the contents are evaporated to dryness. (The titration tube is a tapering tube such as can be made from a centrifuge test-tube. A platinum wire is sealed into the bottom to ensure regular boiling.)

To the tube which now contains a very small residue of salt is added about 1 cc. of water and the resulting solution is acidified by adding three drops of 1% sulfuric acid from a dropping bottle. Three drops of fresh saturated bromine water are added, the solution is evaporated to a volume of about 0.3 cc. and cooled; a minute crystal of potassium iodide is added, and then a small drop of fresh starch solution. The iodine liberated is titrated in good diffuse light with $N/100$ thiosulfate from a micrometer screw buret.[3] If the sample taken contains rather more than 0.4 microgram of iodine, the yellow color of free iodine will be discernible on adding the iodide, and the solution should then be titrated until nearly colorless before adding the starch.

Duplicate analyses by the above method generally agree within 2 to 5% depending on whether the sample has a high or a low iodine content. The reliability of the method has also been checked by testing the recovery of added amounts of iodine. Three identical 25-g. samples of a butter containing 45 micrograms of iodine per kg. were taken and to each of two samples before saponification was added 2 cc. of a solution containing 0.55 microgram of iodine per cc. The three samples were then analyzed with the following result

Sample 1 No iodine added. Contained 1.09 micrograms
Sample 2 1.10 microgram added. Contained 2.16 micrograms
Sample 3 1.10 microgram. Contained 2.16 micrograms

Thus 1.07 or 97% of the iodine added was recovered.

The following are some recent values obtained for butterfats from different places in Otago, New Zealand.

[3] H. A. A. Aitken, *Biochem. J.*, **25**, 446 (1931).

Source	Dunedin	Highcliffe	Kokonga	Momona	Ranfurly
I_2 content, microgram/kg	18	62	21	74	58

As pointed out by the American workers, analyses of butter are of questionable value in the mapping of iodine-efficiency areas on account of the increasing use of iodized dairy feeds and salt licks.

Summary

The iodine content of butterfat may be determined by igniting a relatively small sample with caustic potash, extracting the iodide from the resulting potassium carbonate with alcohol and estimating the iodine by micro-titration using a standard thiosulfate solution.

DUNEDIN, OTAGO, NEW ZEALAND

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

ALLYL LEVULINATE AND ITS DERIVATIVES[1]

BY PETER P. T. SAH AND TSU-SHENG MA

RECEIVED JANUARY 11, 1932 PUBLISHED AUGUST 5, 1932

A number of alkyl levulinates[2] were recently synthesized and studied. Allyl levulinate, representing an unsaturated ester of levulinic acid, has not been reported in the literature. We have successfully prepared this new ester in a very pure condition by direct esterification of levulinic acid[3] with allyl alcohol,[4] using hydrogen chloride as the catalyst. Apparently at low temperature the extent of addition of hydrogen chloride on the ethylene linkage was too slight to affect the yield and the purity of the product. We have further allowed chlorine or bromine to add on the new ester and found the addition products to be identical in physical properties with those obtained by direct esterification of levulinic acid with β,γ-dichloropropyl or β,γ-dibromopropyl alcohol.

To characterize these three new esters, their corresponding semicarbazones and phenylhydrazones were prepared by the usual methods. They were carefully purified and their melting points determined. The experimental details are hereby communicated.

[1] This paper is from a thesis presented by Tsu-Sheng Ma to the Faculty of National Tsinghua University in partial fulfilment of the requirements for the degree of Bachelor of Science, July 1, 1931.

[2] (a) Sah and Ma, THIS JOURNAL, **52**, 4880 (1930); (b) Schuette and Cowley, *ibid.*, **53**, 3485 (1931).

[3] (a) Schuette and Sah, *ibid.*, **48**, 1364 (1926); (b) Thomas and Schuette, *ibid.*, **53**, 2324 (1931).

[4] Kamm and Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, pp. 15–19.

Experimental

Preparation of Allyl Levulinate.—Into a cooled solution of 100 g. of levulinic acid in 200 cc. of allyl alcohol, 15 g. of dry hydrogen chloride was passed. After refluxing, the unesterified alcohol was distilled off on an oil-bath kept at 103°. The residue was fractionated under reduced pressure. The fraction boiling most constantly from 133 to 136° at 40 mm. was collected and purified by vacuum distillation; yield, about 60%.

Freshly distilled in a vacuum, allyl levulinate was a colorless liquid with a faint odor, insoluble in water, but soluble in all organic solvents. Distilled at atmospheric pressure, it boiled with decomposition at 219–222°. The simple physical constants of the pure product were determined and tabulated (see Table I).

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.50; H, 7.75. Found: C, 62.05; H, 8.01.

Addition of Halogens on Allyl Levulinate.—Into a cooled solution of allyl levulinate in carbon tetrachloride, the calculated amount of dry chlorine or bromine was slowly introduced. The solvent was recovered. The residue was fractionated under a reduced pressure of 40 mm. The constant boiling fraction (β,γ-dichloropropyl levulinate at 199–202° and β,γ-dibromopropyl levulinate at 208–210°) was collected and purified by vacuum distillation; yield, about 40% of the theoretical.

Freshly distilled in a vacuum, they were colorless liquids with a faint disagreeable odor, insoluble in water, slightly soluble in carbon disulfide or carbon tetrachloride, but soluble in other organic solvents. Distilled at atmospheric pressure, considerable decomposition took place. The simple physical constants of the pure product were carefully determined and tabulated (see Table I).

To prove the identity of the addition products, β,γ-dichloropropyl[5] and β,γ-dibromopropyl[6] alcohols were prepared and directly esterified with levulinic acid. The esters thus obtained were found to be identical in physical properties to the corresponding addition products from allyl levulinate. For the sake of comparison, the simple physical constants of pure β,γ-dichloropropyl and β,γ-dibromopropyl alcohols were also determined and tabulated (see Table I). The halogen contents of the halogenated esters were determined by Stepanow's method[7] (see Table II).

TABLE I

SIMPLE PHYSICAL CONSTANTS OF REAGENTS AND PRODUCTS

Name	B. p., °C.	d_4^{20}	n_D^{20}	Molecular refraction Gladstone–Dale Obs.	Gladstone–Dale Calcd.	Lorentz–Lorenz Obs.	Lorentz–Lorenz Calcd.
β,γ-Dichloropropyl alcohol	183–185	1.3607	1.4819	45.67	45.70	27.02	27.33
β,γ-Dibromopropyl alcohol	214–215	2.0739	1.5466	57.49	56.28	33.30	33.18
Allyl levulinate	133–136 (40 mm.)	1.0277	1.4413	67.03	67.27	40.14	40.42
β,γ-Dichloropropyl levulinate	199–202 (40 mm.)	1.2357	1.4652	85.46	84.73	50.82	50.71
β,γ-Dibromopropyl levulinate	208–210 (40 mm.)	1.6580	1.5035	95.94	95.31	56.37	56.57

Semicarbazones.[2a]—These were conveniently prepared by shaking the new esters with the calculated amount of semicarbazide hydrochloride and potassium acetate in alcohol solution. They were snow white crystals, insoluble in water. After being dried, their melting points were determined. The semicarbazone of allyl levulinate melted at 126–127°; that of β,γ-dichloropropyl levulinate, at 104–106°; while that of the dibromo analog melted at 101–102°. The nitrogen content of the first was determined by Dumas' method.

Anal. Calcd. for $C_9H_{15}O_3N_3$: N, 19.72. Found: N, 19.59.

[5] King and Pyman, *J. Chem. Soc.*, **105**, 1257 (1914).

[6] Kohler, *Am. Chem. J.*, **42**, 381 (1909).

[7] Stepanow, *Ber.*, **39**, 4056 (1906).

For the dihalogen derivatives, the halogen contents were determined by Stepanow's method (see Table II).

Phenylhydrazones.[2a]—These were easily obtained by shaking the new esters with the calculated amount of phenylhydrazine in ethyl alcohol. The precipitation was instantaneous. The products, recrystallized from benzene and washed with ether, were snow-white crystals. The phenylhydrazone of allyl levulinate melted at 79–80°; that of the dichloro derivative, at 73–75°; and that of the dibromo analog, at 98–99°. The nitrogen content of the first was determined by Dumas' method.

Anal. Calcd. for $C_{14}H_{18}O_2N_2$: N, 11.39. Found: N, 11.6.

For the dihalogen derivatives, again Stepanow's method was used for the determination of their halogen contents (see Table II).

TABLE II

HALOGEN CONTENTS OF DERIVATIVES OF ALLYL LEVULINATE

Name	Formula	Subs., g.	$AgNO_3$ used in cc. (0.1059 *N*)	Halogen, % Found	Calcd.
β,γ-Dichloropropyl levulinate (I)	$C_8H_{12}O_3Cl_2$	0.2503	20.61	30.91	31.23
Phenylhydrazone of I	$C_{14}H_{18}O_2Cl_2N_2$	.2533	15.01	22.24	22.36
Semicarbazone of II	$C_9H_{15}O_3Cl_2N_3$	.2298	15.32	25.03	24.97
β,γ-Dibromopropyl levulinate (II)	$C_8H_{12}O_3Br_2$	.2548	15.15	50.30	50.59
Phenylhydrazone of II	$C_{14}H_{18}O_2Br_2N_2$	.2018	9.46	39.67	39.36
Semicarbazone of II	$C_9H_{15}O_3Br_2N_3$	.3004	15.29	43.07	42.85

Summary

1. Allyl levulinate, a new ester, was prepared by the direct esterification of levulinic acid with allyl alcohol in the presence of hydrogen chloride.

2. Direct chlorination or bromination of allyl levulinate yielded β,γ-dichloropropyl or β,γ-dibromopropyl levulinates, identical with the products obtained by the direct esterification of levulinic acid with β,γ-dichloropropyl or β,γ-dibromopropyl alcohol.

3. The simple constants of β,γ-dichloropropyl alcohol, β,γ-dibromopropyl alcohol, and the three new esters of levulinic acid were determined.

4. The three new esters were characterized by their corresponding semicarbazones and phenylhydrazones.

PEIPING-WEST, CHINA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE COMMON BASIS OF INTRAMOLECULAR REARRANGEMENTS[1]

BY FRANK C. WHITMORE

RECEIVED JANUARY 12, 1932 PUBLISHED AUGUST 5, 1932

The failure of organic reactions to give yields approaching the theoretical is well known. Processes which deviate most from the theoretical involve either an apparent metathesis or the elimination of an inorganic molecule such as water, halide acid or nitrogen. These reactions are also the chief source of the rearrangements which have become so common in organic chemistry. In the years since Fittig discovered the pinacolone rearrangement,[2] countless other rearrangements have been found and many explanations have been evolved.[3] These explanations have assumed intermediates including cyclopropane rings, ethylene oxide rings, olefins, univalent nitrogen, bivalent carbon, ordinary ions, bipolar ions and chelate compounds.

The purpose of this paper is to show that rearrangements and the peculiarities of organic "metathetical" reactions have a common mechanism based on the very nature of the "bonds" in organic compounds as contrasted to the ionic attachments in inorganic molecules. All the essentials of the mechanism proposed in this paper are old and are implicit in conceptions of atoms and molecules introduced during the last twenty years by G. N. Lewis, Arthur Michael, Julius Stieglitz, Lauder W. Jones, W. A. Noyes, Hans Meerwein, H. J. Lucas and Charles Prévost. In each

[1] An abstract of a paper presented at the Fourth Symposium on Organic Chemistry of the American Chemical Society, New Haven, Conn., Dec. 30, 1931. See pp. 3431–3454.

[2] Fittig, *Ann.*, **114**, 56 (1860).

[3] The following give the more recent work in this field: "Chem. Soc. Ann. Rep.," 1923, p. 115; 1924, p. 96; 1925, p. 116; 1927, pp. 115, 133; 1928, p. 133; 1930, pp. 114–124. Meerwein and co-workers, *Ann.*, **435**, 190 (1924); **453**, 32 (1927); **455**, 227 (1927); Michael, THIS JOURNAL, **42**, 787 (1920); Tiffeneau and co-workers, *Bull. soc. chim.*, [4] **27**, 459, 782 (1920); Lévy, *ibid.*, [4] **29**, 865 (1921); Stieglitz, THIS JOURNAL, **44**, 1294 (1922); Robinson (Ingold), *J. Chem. Soc.*, **123**, 1706 (1923); Ruzicka, *Helv. Chim. Acta*, **6**, 276 (1923); Lucas, Simpson and Carter, THIS JOURNAL, **47**, 1465 (1925); McKenzie, and co-workers, *J. Chem. Soc.*, 779 (1926); Stewart and Aston, THIS JOURNAL, **49**, 1718 (1927); Shoppee, *Brit. Chem. Abstracts*, [A] 1135 (1928); Porter, "Molecular Rearrangements," A. C. S. Monograph, The Chemical Catalog Co., New York, 1928; Ramart-Lucas, *Bull. soc. chim.*, [4] **45**, 718 (1928); Latimer, THIS JOURNAL, **51**, 3185 (1929); Hückel, *Ann.*, **477**, 156 (1930); Prévost and Kirrmann, *Bull. soc. chim.*, [4] **49**, 212, 240 (1931); Bergmann and Schuchardt, *Ann.*, **487**, 225 (1931); Hückel, "Theoretische Grundlagen der organischen Chemie," Leipzig, 1931, Vol. I, pp. 205–251; Tiffeneau and co-workers, *Bull. soc. chim.*, [4] **49**, 1595–1874 (1931); Ramart-Lucas and Amagat, *ibid.*, [4] **51**, 108 (1932); Bachmann, THIS JOURNAL, **54**, 1124, 2112 (1932).

case circumstances limited the application of these conceptions. The time has arrived, however, when the multitude of explanations of organic rearrangements can be discarded and the fact must be realized that these interesting reactions are not merely freaks to be expected from certain complex compounds but are dependent on properties inherent in even the simplest organic molecules. As soon as this important fact is recognized, it will be possible to focus attention on the fundamental changes taking place in all rearrangements instead of considering each type of rearrangement as an isolated exception. Even such simple processes as the formation of tertiary butyl halides from isobutyl alcohol will be found to follow the same course as the pinacolone rearrangement.[4]

The first recognition of the true cause of an intramolecular rearrangement was achieved independently by Julius Stieglitz and Lauder W. Jones about 1913 in connection with the rearrangements of organic nitrogen compounds.[5] Jones says of the Hofmann conversion of N-bromoamides to isocyanates and amines: "The present mode of viewing the rearrangement would speak of the potency of the carbon atom to lose negative electrons and of the nitrogen atom to acquire them, and would look upon the free valences of univalent nitrogen as the stage setting required to furnish a suitable environment in which the essential action may take place."

In considering the rearrangement of triphenylmethyl hydroxylamine and its relation to the Hofmann, Lossen and Curtius rearrangements, Stieglitz states, "In the formation of water, containing the stable negative hydroxyl, the oxime hydroxyl deprives the nitrogen atom of two electrons. . . ." In 1916, referring to the same types of rearrangements, he said, "In recent years the initial force leading to the rearrangements has been sharply defined, on the basis of the electron theory of valence, as residing in the instability of the charges on the radicals held by nitrogen . . . and to the great tendency of these radicals to go over into their stable forms . . . by absorption of electrons from neighboring atoms. . . ."[6]

The conception of bivalent carbon as an intermediate in rearrangements has been used by many including Nef, Tiffeneau, Lucas and, most recently, Hellerman,[7] who combines the bivalent carbon assumption with a transfer

[4] See pp. 3279, 3448.

[5] Jones, *Am. Chem. J.*, **50**, 441 (1913); Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914); Stieglitz and Stagner, *ibid.*, **38**, 2047 (1916); *Cf. Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); *Proc. Natl. Acad. Sci.*, **1**, 207 (1915).

[6] After this paper was presented at New Haven, a colleague of Dr. Stieglitz informed the author that similar conceptions had been applied to C—C rearrangements by Dr. Stieglitz in his advanced classes for several years. Since the meeting Dr. Stieglitz has kindly made available unpublished theses by R. B. Cooper, 1930, and G. W. Ayer, 1931, in which oxonium salts of pinacol are prepared and a mechanism for the rearrangement is proposed which is entirely analogous to that of the present paper. See also the Dohme Lecture by Dr. Stieglitz at Johns Hopkins University, February 19, 1932.

[7] Hellerman, THIS JOURNAL, **50**, 1718 (1928).

of electrons. The bivalent carbon mechanism could not be applied to tertiary alcohols or related compounds. P. A. Krueger of this Laboratory has called attention to the fact that the assumption of bivalent carbon will not account for the facts even with a secondary alcohol like pinacolyl alcohol which gives tetramethylethylene and *unsym.*-methylisopropylethylene on dehydration, whereas the assumption of bivalent carbon would indicate tetramethylethylene and *tert.*-butylethylene as the products to be expected.

In recent years Meerwein and his co-workers have added materially to our knowledge of rearrangements and have shown that conditions which favor ionization also favor rearrangement in many cases. In certain cases they have proved that it is the positive ion which undergoes rearrangement rather than the molecule.[8] The present study is an extension of this work but is not limited to cases in which ordinary ionization is possible.[9]

The English school of organic chemists, including Robinson, Ingold, Shoppee and their students, has long emphasized the dependence of various types of rearrangements on electron transfer within the molecule.[10]

The present study involves, then, a fusion and a simplification as well as a more general application of much that has gone before. Most organic molecules which give poor yields of "metathetical" products, or of products obtained by elimination of an inorganic molecule, or which give rearranged products, contain a portion which can be indicated electronically in one of the following ways



(1) (2)

in which X is usually oxygen or halogen or other strongly electronegative atom and A, B and D are atoms like carbon and nitrogen which are neither strongly electronegative nor strongly electropositive. In the original compound, each atom has a completed octet of electrons and the linking is due to the shared electrons. These compounds are usually very stable and relatively inactive. They remain so only while all the octets are complete. System (1) is involved in such "two atom" rearrangements, as the pinacolic, the retropinacolic, the Hofmann, the Beckmann and many others, some of which have been named and some of which stand merely as isolated abnormalities of organic chemistry. System (2) is found in many types of allylic or triad rearrangements.

When a molecule containing System (1) is brought into a reaction which results in the *removal of X*[11] from its attachment to atom B, then, *regardless*

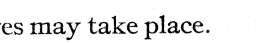
[8] *Cf.* Lipp, *Ber.*, **65**, 242 (1932).

[9] See p. 3441.

[10] See "Annual Reports of the Chemical Society" since 1923.

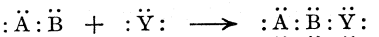
[11] This point in the present hypothesis called forth much criticism from the referees. In some reactions the first step appears to be an actual ionization (Meerwein) but, more often, it involves the formation of an addition compound such as an oxonium salt which is then decomposed to form the final products. The entire process behaves more

of the mechanism of the process, X keeps a complete octet of electrons and leaves B with only a sextet of electrons, an "open sextet" (Prévost). Thus at some instant System (1) becomes



Three different changes may take place.

1. The positive organic fragment,[12] depending on the chemical nature and environment of A and B, may have a life long enough to allow it to combine with a negative ion Y in the reaction mixture.



In such a case, the reaction is "normal," no rearrangement takes place, and the process resembles the simple metathetical reactions of inorganic chemistry. It is not usual for an organic reaction to follow this course entirely.

2. If the atom A has a hydrogen attached to it, the fragment can be stabilized by the loss of a proton.

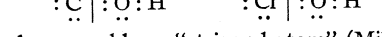


The product is an olefin or other unsaturated molecule.[13] This process is very common in organic reactions and has led many to believe that the olefin is an intermediate product in such reactions instead of merely a by-product.[13a]

3. The nature and environment of A and B may be such that B has the greater attraction for electrons or that A can more readily dispense with a pair of its electrons. In either case a change in the fragment will leave A with an open sextet.

like an activation than an ordinary ionization. It might be assumed that a single molecule suffers the separation of the ion X with a complete octet, leaving the rest of the molecule deficient in electrons. This residue then undergoes a change which liberates energy and "activates" another molecule. One of the simplest sources of energy in such a system would be the loss of a proton and the formation of an olefinic linkage. This may account for the common formation of olefins in reactions which might be expected to be simple metatheses (see p. 344).

[12] This positive organic "ion" differs from ordinary positive ions which contain completed electron shells. It resembles the "Cl^+ ion" which is indicated by certain reactions of hypochlorous acid. The analogy is significant.



The positive organic ion also resembles a "stripped atom" (Millikan) more than it does an ordinary ion. The extraordinary instability of such an "ion" accounts for many of the peculiarities of organic reactions.

[13] Just as a proton in the 2 position to the positive carbon can be eliminated with the formation of an olefinic linkage, so a proton in the 5 or 6 position might be eliminated with the formation of a 5- or 6-membered ring. This is what happens in the formation of indene derivatives by a rearrangement which has been published since this paper was presented [Ottilie Blum-Bergmann, *Ber.*, **65**, 109 (1932)].

[13a] See pp. 3442, 3448.



The shift of the electron pair includes the atom or group which it holds.

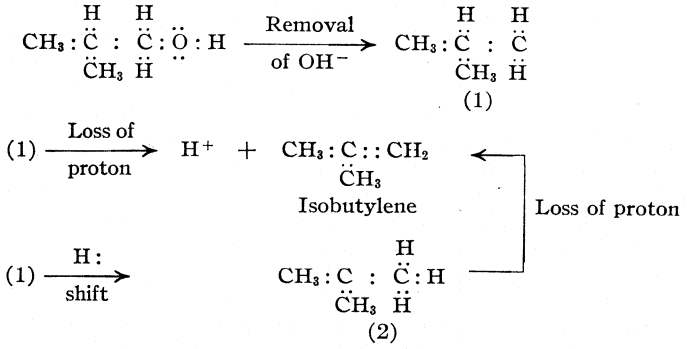
The new fragment can then recombine with the ion X or with a new negative ion Y from the reaction mixture. The result is an "abnormal" or rearranged product, the series of changes being



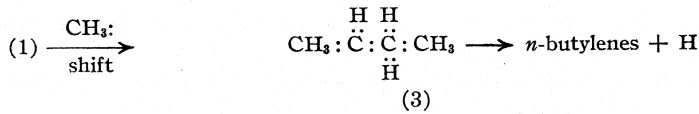
If atom B in the rearranged positive fragment has a hydrogen attached to it, the system may lose a proton. Depending on the other groups attached to A and B, the resulting unsaturated compound may or may not be identical with that obtained by the loss of a proton from the original fragment. It is important to note that the shift of electrons within the positive fragment and the stabilization by loss of a proton are *monomolecular* processes which may effectively compete with the *bimolecular* union of the original or the rearranged fragment with an ion from the reaction mixture. Thus the formation of considerable amounts of abnormal products is to be expected.

A study of these fundamental changes shows that processes in which a strongly electronegative atom or group is *removed* from an organic molecule during a reaction may readily give products other than those of simple metathetical or elimination reactions. Such a conclusion agrees with the facts. This simple mechanism fits all types of rearrangements which involve the transfer of an atom or group from one atom to an adjacent one. Its application is shown by the following examples.

The dehydration of isobutyl alcohol gives *normal* butylenes as well as the expected isobutylene.[14]



[14] Nevole, *Bull. soc. chim.*, [2] **24**, 122 (1875); Le Bel and Greene, *ibid.*, [2] **29**, 306 (1878); *Am. Chem. J.*, **2**, 23 (1880); Konowalow, *Ber.*, **13**, 2395 (1880); *Bull. soc. chim.*, [2] **34**, 333 (1880); Faworski and Debout, *J. prakt. Chem.*, [2] **42**, 153 (1890); Wislicenus and Schmidt, *Ann.*, **313**, 210 (1900); Nef, *ibid.*, **318**, 211 (1901); Ipatiew, *Ber.*, **35**, 1061 (1902); **36**, 1997, 2011 (1903); Senderens, *Bull. soc. chim.*, [4] **1**, 693 (1907); *Ann. chim. phys.*, [8] **25**, 497 (1912); similar results have been obtained in this Laboratory by J. C. Mitchell using a phosphoric acid catalyst at 250°.

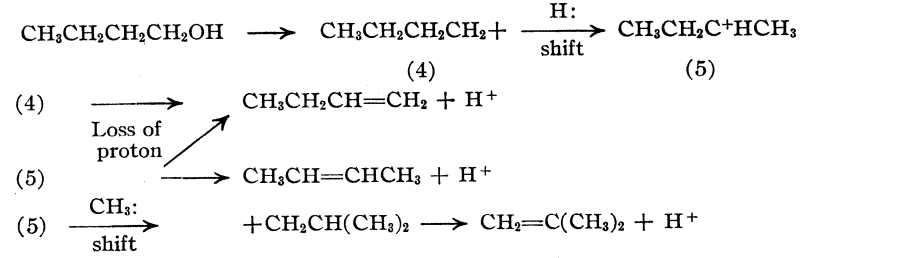


(3)

In a similar way isobutyl iodide reacts with lead oxide to give both isobutylene and butene-2.[15]

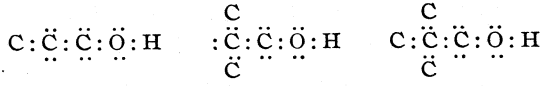
If instead of dehydrating isobutyl alcohol, it is treated with hydrobromic acid, the product is not pure isobutyl bromide but contains tertiary butyl bromide (Michael). Under the conditions, only fragments (1) and (2) are formed in effective amounts. In other words, only hydrogen rearranges. At higher temperatures and with dehydrating catalysts fragment (3) is formed in large amounts by the shift of a methyl.

The dehydration of *normal* butyl alcohol gives isobutylene and all three normal butylenes instead of only the expected butene-1.[16] The probable steps in this process follow. For the sake of simplicity the atom in an open sextet is indicated by a + without any assumption as to its ionic properties.



Exactly similar changes take place during the dehydration of secondary butylcarbinol to give mainly trimethylethylene and small amounts of pentene-2 and *unsym.*-methylethylethylene.[17]

The tendency to rearrangement increases with the number of carbon atoms attached to "A" in the two atom system.



Thus compounds containing the last of these systems, the "neopentyl alcohol" system, give mainly rearrangement products in any reaction in which the hydroxyl is removed. They give esters of organic acids without rearrangement but all attempts to replace the hydroxyl by halogen lead to rearranged products.[18] Thus neopentyl alcohol itself (tertiary butylcar-

[15] Eltekow, *Ber.*, **13**, 2404 (1880).

[16] Senderens, *Bull. soc. chim.*, [4] **1**, 692 (1907). Lucas was unable to obtain any isobutylene from butanol-1 or -2 (private communication).

[17] Wischnegradsky, *Ann.*, **190**, 350 (1877); Étard, *Compt. rend.*, **86**, 488 (1878); Kondakow, *Ber.*, **25**, Ref. 570 (1892); Tissier, *Ann. chim. phys.*, [6] **29**, 326 (1893).

[18] Beilstein, 4th ed., Vol. I, p. 152, Spl. Vol. I, p. 54; Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1487 (1929).

binol) gives tertiary amyl halides and olefins formed from the rearranged fragment. The alcohol of this type which has been most studied is pinacolyl alcohol (methyl-tertiary-butylcarbinol) which gives none of the expected tertiary butylethylene on dehydration but only the rearranged products, tetramethylethylene and *unsym.*-methylisopropylethylene. Attempts to convert pinacolyl alcohol to the corresponding halide also give only rearranged products.[19]

An even more surprising failure to give a "normal" dehydration is shown by isopropyl-tertiary-butylcarbinol[20] which gives none of the expected product, 2,2,4-trimethylpentene-3.[21] In this case, the loss of a tertiary hydrogen to give an olefin is more difficult than the shift of a methyl group and its electron pair from the neopentyl system. A case in which the hydroxyl of the neopentyl alcohol system is tertiary and has no alpha hydrogens is presented by diphenyl-tertiary-butylcarbinol.[22] This substance is dehydrated with extraordinary ease to give 2,2-diphenyl-3-methylbutene-3 with the shift of a methyl group. On the other hand, a purely aliphatic neopentyl alcohol with a tertiary hydroxyl, methylethyltertiarybutylcarbinol[23] gives the "normal" dehydration product, and a lesser amount of the rearranged product.

The rearrangement of borneol to camphene and the many similar rearrangements in the terpene and other series studied so brilliantly by Meerwein follow this same course.[24] In each case the open sextet left after removal of the hydroxyl or halogen is completed by the transfer of an electron pair from an adjacent carbon with the corresponding shift of a carbon–carbon linkage.

The pinacolone rearrangement and rearrangements of other types of glycols, iodohydrins and related compounds follow a similar course. The more reactive hydroxyl or halogen atom is removed in the course of the reaction, leaving an open sextet which is completed by a rearrangement. An interesting variant of this reaction is the conversion of isobutylene dibromide and trimethylethylene dibromide into isobutyraldehyde and methyl isopropyl ketone by merely heating with water.[25] In each case the

[19] These results with neopentyl alcohol and pinacolyl alcohol have been entirely confirmed in this Laboratory, see p. 3431.

[20] Unpublished results of A. L. Houk of this Laboratory.

[21] This substance has been separated from "di-isobutylene" and its properties determined for identification purposes; Whitmore and Wrenn, THIS JOURNAL, **53**, 3136 (1931), and unpublished results of C. O. Tongberg, J. D. Pickens and J. M. Church of this Laboratory.

[22] Ramart-Lucas, *Compt. rend.*, **179**, 634 (1924); Marvel and Bateman, THIS JOURNAL, **49**, 2914 (1927).

[23] Unpublished results of K. C. Laughlin of this Laboratory.

[24] Meerwein, *Ber.*, **53**, 1815 (1920); **55**, 2500, 2533 (1922); *Ann.*, **453**, 16 (1927).

[25] Unpublished results by H. S. Rothrock and W. L. Evers of this Laboratory; *cf.* Eltekow, *J. Russ. Phys.-Chem. Soc.*, **10**, 215 (1878); Froebe and Hochstetter, *Monatsh.*, **23**, 1075 (1902).

tertiary bromine is removed with its octet and a hydrogen with its electron pair shifts.

The conversion of aliphatic amines to alcohols by treatment with nitrous acid is unusually subject to side reactions.[26] Thus isobutylamine gives mainly tertiary butyl alcohol and isobutylene.[27] In this case the intermediate product loses a hydroxyl or other ion with a complete octet and a nitrogen molecule with its ten electrons, thus leaving a carbon with an open sextet which makes possible the usual rearrangement.[28] Interesting cases of this rearrangement are the conversion of cyclopropylamine into allyl alcohol by nitrous acid[29] and the Demjanow rearrangement[30] which has recently been shown by Fuson[31] to take place with aliphatic as well as with alicyclic amines.

The rearrangements of Hofmann, Lossen, Curtius and Beckmann all involve the system

$$R:\ddot{C}:\ddot{N}:\ddot{X}: \quad \text{or} \quad R:\ddot{C}::\ddot{N}:\ddot{X}:$$

If X is removed with its octet in the course of the reaction, a rearrangement of R: takes place in the usual way.[32]

$$R:\ddot{C}:\ddot{N} \longrightarrow \ddot{C}:\ddot{N}:R \qquad R:\ddot{C}::\ddot{N} \longrightarrow \ddot{C}::\ddot{N}:R$$

The resulting product, depending on the groups involved and the conditions of the reaction, is an isocyanate, an amine, or a substituted amine. In certain types of compounds, X is sometimes removed with only a sextet of electrons (as positive halogen by hydrolysis) and the remaining fragment has a complete octet and consequently cannot rearrange. J. G. Aston of this Laboratory was the first to recognize that the shifting group in the Hofmann and related rearrangements cannot rearrange internally during its transfer from carbon to nitrogen because it has its full complement of electrons during this transfer. This prediction has been strikingly confirmed in the case of the amide of *tert.*-butylacetic acid.[33]

Although rearrangement of compounds containing carbonyl groups and no group corresponding to the X in the systems discussed so far might be expected to follow a very different course, such may not be the case. The only difference is that an atom with an open sextet may be formed by

[26] Hellerman, THIS JOURNAL, **50,** 1718 (1928); Hellerman and Garner, "Aliphatic Diazo Compounds. II," Buffalo Meeting, American Chemical Society, September 3, 1931.

[27] Linnemann, *Ann.*, **162,** 24 (1872); Henry, *Compt. rend.*, **145,** 899 (1907).

[28] See p. 3141.

[29] Kishner, *J. Russ. Phys.-Chem. Soc.*, **37,** 317 (1905).

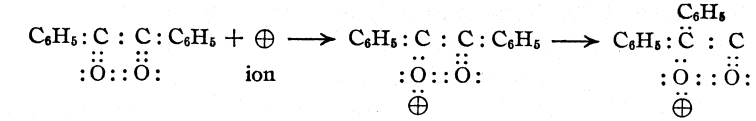
[30] Demjanow, *Ber.*, **40,** 4397 (1907).

[31] Private communication.

[32] In the Curtius rearrangement of acid azides, triarylmethyl azides and benzyl azide, X is a pair of nitrogen atoms with ten electrons.

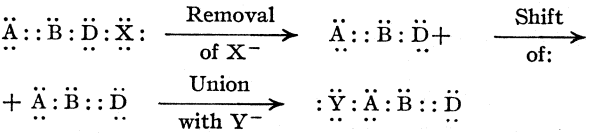
[33] See p. 3436.

the *addition* of a positive ion instead of by the *removal* of a negative ion. Thus the first step in the benzilic acid rearrangement becomes



The carbon with the open sextet then attracts the electron pair and phenyl group from the adjacent carbon. Addition of an hydroxyl ion to the rearranged fragment converts it to benzilic acid. A similar result is obtained in the conversion of trisubstituted acetaldehydes to ketones by concentrated sulfuric acid.[34] The initial addition product of the aldehyde with a proton undergoes rearrangement because of an open sextet and then loses a proton to give the enolic form of the ketone.

The rearrangements in triad systems which have been studied so intensively in recent years, especially by the English school of organic chemists, involve similar changes.[35] Thus



My sincere thanks are due my colleagues, J. G. Aston, P. A. Krueger and R. V. McGrew, for their help and criticisms in the development of this work. Special recognition is due Dr. McGrew for his help in the direction of the experimental studies on which the accompanying papers are based.[36]

Summary

Many of the "abnormal" reactions of organic chemistry, including most intramolecular rearrangements, are correlated by the following simple assumptions.

1. A non-ionic attachment between an atom like carbon or nitrogen and an electronegative atom or group *is broken during the reaction.*

2. At the instant of removal of the electronegative group, it takes a completed octet of electrons with it.

3. The atom which had shared an electron pair with the electronegative group is thus left with only a sextet of electrons.

4. This deficiency of two electrons may induce a migration of an electron pair from an adjacent atom, thus giving rise to "abnormal" or rearranged products.

[34] Tiffeneau and Orékhoff, *Compt. rend.*, **182,** 67 (1926); Danilov, *Ber.*, **60,** 2390 (1927); Ramart-Lucas and Guerlain, *Bull. soc. chim.*, [4] **49,** 1860 (1931).

[35] For summaries and references see Prévost, *Compt. rend.*, **184,** 1460 (1927); Ingold and Burton, *J. Chem. Soc.*, 904 (1928); Ingold and Shoppee, *ibid.*, 1199 (1929); Ingold, *ibid.*, 2752 (1931).

[36] See pp. 3431–3454.

5. In the case of carbonyl compounds a carbon with an open sextet may be formed by the addition of a positive ion to the oxygen. In this case also the presence of the open sextet induces rearrangement.

6. The application of these simple principles is already proving helpful in experimental studies of "abnormal" reactions of simple aliphatic compounds.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. I

BY C. B. POLLARD, C. E. SPARKS AND M. L. MOORE

RECEIVED MARCH 4, 1932 PUBLISHED AUGUST 5, 1932

When diacyl derivatives of *o*-aminophenol were prepared by the usual methods, it was found in many cases that the order of introduction of the two different acyl groups has no influence upon the formation of the diacyl, identical products being isolated from the two acylations. The position of the acyl groups can be determined by removing the groups attached to the oxygen by saponification with dilute alkali, and determining from the physical constants of the remaining monoacylated product the group attached to the nitrogen. The identical diacyls mentioned above were found to saponify to yield identical products, as would be expected.

The formation of identical rather than isomeric products on reversing the order of acylation indicated that during acylation a rearrangement must have occurred in one of the two cases. The formation of isomeric diacyls and the production of the same saponification product indicate that a rearrangement must have occurred during saponification. Some evidence has indicated that certain acyl groups have more power than others to bring about this migration, weight and acidity of the groups being considered to have the predominating influence in their obtaining a position in the more basic amino group.

Previous work on this subject by Ransom,[1] Ransom and Nelson,[2] Nelson and Rothrock,[3] and Raiford and Clark[4] is discussed in the literature.

The work of Pollard and Nelson,[5] using phenylacetyl chloride as one of the acylating agents in each diacyl throughout a series of experiments, indicated that relative acidity and weight are not the controlling factors in this type of rearrangement.

[1] Ransom, *Am. Chem. J.*, **23**, 1 (1900).

[2] Ransom and Nelson, THIS JOURNAL, **36**, 390 (1914).

[3] Nelson and Rothrock, *ibid.*, **51**, 2761 (1929).

[4] Raiford and Clark, *ibid.*, **48**, 483 (1926).

[5] Pollard and Nelson, *ibid.*, **53**, 996 (1931). A more extensive bibliography is given in this article.

To determine whether similar results would be obtained by using the hydrocinnamyl group as a constant was the purpose of this investigation. Hydrocinnamyl chloride was used as one of the acylating agents in the preparation of all diacyl derivatives of *o*-aminophenol in these experiments. This selection afforded a rather heavy group and one which is appreciably acidic in nature to check against the acetyl, propionyl, valeryl, isovaleryl, phenylacetyl and benzoyl groups.

When *o*-hydrocinnamylaminophenol was acylated with acetyl chloride, a diacyl melting at 79.5–81° was produced, while the acylation of *o*-acetylaminophenol with hydrocinnamyl chloride gave a diacyl melting at 124.5–126°. Saponification of each of these diacyls produced only *o*-hydrocinnamylaminophenol, indicating that in the latter case migration of the hydrocinnamyl group from the oxygen to the nitrogen must have occurred. Similar results were obtained with diacyls containing, respectively, the valeryl, isovaleryl and benzoyl groups. The saponification of these isomers involved rearrangements in which the hydrocinnamyl group replaced the lighter and less acidic valeryl and isovaleryl and the lighter and more acidic benzoyl group.

o-Hydrocinnamylaminophenol acylated with propionyl chloride gave a diacyl melting at 113.5–115.5°, while the acylation of *o*-propionylaminophenol with hydrocinnamyl chloride gave a diacyl melting at 102.5–104.5°. A mixture of these two products melted at 110–115°, indicating that each might be an equilibrium mixture of the two possible diacyls. However, each product gave only *o*-hydrocinnamylaminophenol on saponification.

Acylation of *o*-hydrocinnamylaminophenol with phenylacetyl chloride gave a diacyl melting at 90–92°, while acylation of *o*-phenylacetylaminophenol with hydrocinnamyl chloride gave a diacyl melting at 81–83°. A mixture of these two products melted at 67–70°, showing the two to be different. Saponification of each of these diacyls gave approximately 60% *o*-hydrocinnamylaminophenol and 40% *o*-phenylacetylaminophenol, showing that a partial rearrangement occurred.

Experimental

o-Hydrocinnamylaminophenol was prepared by the method of Groenvik[6] using *o*-aminophenol and the acid chloride. Its properties are summarized below.

Formula	M. p., °C.	Yield, %	Analysis, N, % Calcd.	Found
$HOC_6H_4NHCOCH_2CH_2C_6H_5$	131.5–132	70	5.81	5.65

The other monoacyls used, which have been described previously, were made by the same method.

o-Hydrocinnamylaminophenyl Acetate ($C_6H_5CH_2CH_2CONHC_6H_4OCOCH_3$).—To 5 g. of *o*-hydrocinnamylaminophenol an excess of acetyl chloride was added. After the addition of a drop of sulfuric acid, the mixture was stirred and heated on the water-bath

[6] Groenvik, *Bull. soc. chim.*, [2] **25**, 173 (1876).

for three hours. A brown oil formed which was washed well with hot water and upon cooling in an ice bath solidified. This brown solid was dissolved in hot 90% alcohol and filtered. Repeated crystallizations from dilute alcohol gave light tan crystals melting at 79.5–81°.

About 1 g. of this compound was saponified in the equivalent quantity of 10% potassium hydroxide. After complete solution resulted, the solution was filtered and acidified with dilute hydrochloric acid. A flesh-colored precipitate formed which was filtered, washed and crystallized from dilute alcohol. These crystals melted at 129.5–131° and when mixed with *o*-hydrocinnamylaminophenol (m. p. 131.5–132°) melted at 130–131.5°, showing them to be the same.

***o*-Acetylaminophenyl Hydrocinnamate** ($CH_3COHNC_6H_5OCOCH_2CH_2C_6H_5$).—A slight excess of hydrocinnamyl chloride was added to 6 g. of *o*-acetylaminophenol. A drop of sulfuric acid was added, the mixture stirred and heated on the water-bath for two hours. A light brown oil formed which was washed well with hot water and cooled in an ice-bath. On standing the oil solidified. The solid was dissolved in hot alcohol and on cooling formed light pink flakes. These were recrystallized from dilute alcohol and then from toluene. These crystals melted at 124.5–126°.

TABLE I

DIACYL DERIVATIVES OF *o*-AMINOPHENOL

	Name	Formula
1	*o*-Hydrocinnamylaminophenyl acetate	$C_6H_5CH_2CH_2CONHC_6H_4OCOCH_3$
2	*o*-Acetylaminophenyl hydrocinnamate	$CH_3CONHC_6H_4OCOCH_2CH_2C_6H_5$
3	*o*-Hydrocinnamylaminophenyl propionate	$C_6H_5CH_2CH_2CONHC_6H_4OCOC_2H_5$
4	*o*-Propionylaminophenyl hydrocinnamate	$C_2H_5CONHC_6H_4OCOCH_2CH_2C_6H_5$
5	*o*-Hydrocinnamylaminophenyl valerate	$C_6H_5CH_2CH_2CONHC_6H_4OCOC_4H_9$
6	*o*-Valerylaminophenyl hydrocinnamate	$C_4H_9CONHC_6H_4OCOCH_2CH_2C_6H_5$
7	*o*-Hydrocinnamylaminophenyl isovalerate	$C_6H_5CH_2CH_2CONHC_6H_4OCOC_4H_9$
8	*o*-Isovalerylaminophenyl hydrocinnamate	$C_4H_9CONHC_6H_4OCOCH_2CH_2C_6H_5$
9	*o*-Hydrocinnamylaminophenyl phenylacetate	$C_6H_5CH_2CH_2CONHC_6H_4OCOCH_2C_6H_5$
10	*o*-Phenylacetylaminophenyl hydrocinnamate	$C_6H_5CH_2CONHC_6H_4OCOCH_2CH_2C_6H_5$
11	*o*-Hydrocinnamylaminophenyl benzoate	$C_6H_5CH_2CH_2CONHC_6H_4OCOC_6H_5$
12	*o*-Benzoylaminophenyl hydrocinnamate	$C_6H_5CONHC_6H_4OCOCH_2CH_2C_6H_5$

	M. p., °C.	Yield, %	Analyses, N, % Calcd.	Found	Saponification product
1	79.5–81	51	4.97	5.25	$C_6H_5CH_2CH_2CONHC_6H_4OH$
2	124.5–126	67	4.97	5.07	$C_6H_5CH_2CH_2CONHC_6H_4OH$
3	113.5–115.5	55	4.69	4.58	$C_6H_5CH_2CH_2CONHC_6H_4OH$
4	102.5–104.5	84	4.69	4.70	$C_6H_5CH_2CH_2CONHC_6H_4OH$
5	74–75.5	85	4.32	4.18	$C_6H_5CH_2CH_2CONHC_6H_4OH$
6	72.5–74	52	4.32	4.18	$C_6H_5CH_2CH_2CONHC_6H_4OH$
7	92–93	84	4.32	4.50	$C_6H_5CH_2CH_2CONHC_6H_4OH$
8	73.5–74	52	4.32	4.25	$C_6H_5CH_2CH_2CONHC_6H_4OH$
9	90–92	30	3.90	3.90	60% $C_6H_5CH_2CH_2CONHC_6H_4OH$ 40% $C_6H_5CH_2CONHC_6H_4OH$
10	81–83	45	3.90	4.05	60% $C_6H_5CH_2CH_2CONHC_6H_4OH$ 40% $C_6H_5CH_2CONHC_6H_4OH$
11	116.5–118.5	55	4.06	4.05	$C_6H_5CH_2CH_2CONHC_6H_4OH$
12	122.5–124.5	44	4.06	4.20	$C_6H_5CH_2CH_2CONHC_6H_4OH$

This diacyl was saponified in approximately the same manner as the preceding one and yielded *o*-hydrocinnamylaminophenol. A rearrangement must have occurred during saponification.

All diacyl derivatives of *o*-aminophenol were made by the method described above using the monoacyl, the acid chloride and a drop of sulfuric acid, which is a modification of the method of Jacobs, Heidelberger and Rolf.[7] The properties of all of these diacyls are summarized in Table I.

The melting points in the cases of two pairs of isomers listed above as 5, 6, 11 and 12 might indicate the possibility that in each case they were identical substances in an impure state, but the facts that each substance appeared to be homogeneous and the melting points of the mixtures were decidedly lower lead to the conclusion that they were isomers.

Mixed melting point of 5 and 6	52–54°
Mixed melting point of 11 and 12	90–93°

Summary

A study of the diacyl derivatives of *o*-aminophenol, when one of the acyl groups was always the hydrocinnamyl radical, has been made. The hydrocinnamyl group was checked against the acetyl, propionyl, valeryl, isovaleryl, phenylacetyl and benzoyl groups.

In five cases out of six, isomers were obtained depending on the order of introduction of the acyl groups.

In five cases out of six, complete rearrangement occurred during saponification and one case showed partial rearrangement. When complete rearrangement did occur the nitrogen atom was shown to be attached to the heavier and more acidic group in four cases and to the heavier and less acidic in one case.

In the case where partial rearrangement occurred during saponification, the saponification products showed 60% of the nitrogen to be attached to the heavier and less acidic group and 40% to be attached to the lighter and more acidic group.

New mono and diacyl derivatives of *o*-aminophenol have been made and studied.

GAINESVILLE, FLORIDA

[7] Jacobs, Heidelberger and Rolf, THIS JOURNAL, **41**, 458 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDIES OF ORGANIC LEAD COMPOUNDS. III. THE REACTION OF ORGANIC LEAD SALTS ON MERCURY AND LEAD ARYLS

BY PAUL R. AUSTIN[1]

RECEIVED MARCH 7, 1932 PUBLISHED AUGUST 5, 1932

Various metallic and organo-metallic halides have been arylated by means of mercury derivatives[2] and it was thought that this reaction might be utilized in the synthesis of organic lead compounds as follows

$$R_2PbX_2 + R_2Hg \longrightarrow R_3PbX + RHgX$$

Diphenyllead dichloride and diphenylmercury heated in pyridine gave a 21% yield of triphenyllead chloride. Phenylmercuric chloride was easier to isolate and a 57% yield was obtained. When the following reaction $(o\text{-}C_7H_7)_2PbCl_2 + (C_6H_5)_2Hg \longrightarrow (o\text{-}C_7H_7)_2(C_6H_5)PbCl + (C_6H_5)HgCl$, was carried out in an attempt to obtain mixed compounds, phenylmercuric chloride was obtained in a 38% yield, but the expected phenyldi-*o*-tolyllead chloride could not be isolated from the mixture of reaction products. A small amount of diphenyllead dichloride which was isolated indicated that a further reaction had taken place.

Triphenyllead chloride when refluxed with diphenyl- or dibenzylmercury in a variety of solvents did not react. A small amount of tetraphenyllead was formed in every case, but a study of the decomposition of trialkyl and triaryl lead halides on heating showed that the tetraphenyllead resulted from disproportionation according to the equation

$$R_3PbCl \rightleftharpoons R_2PbCl_2 + R_4Pb$$

a type of reaction which has been previously observed in the pyrolysis of triethyllead bromide[3] and triphenyltin hydroxide.[4] Triphenyllead chloride heated in butyl alcohol yielded about 10% of the expected compounds. Similar results were obtained when triethyllead chloride was heated in toluene or benzene. These yields suggested that the reaction might be reversible when carried out in organic solvents. This was found to be the case and tetraphenyllead and diphenyllead dichloride heated in butyl alcohol gave an 86% yield of triphenyllead chloride. Tetraethyllead and diethyllead dichloride heated in benzene gave a 39% yield of triethyllead chloride. Tetraphenyllead and di-*o*-tolyllead dihalides heated in benzene or toluene in an attempt to form a mixed aryl lead halide did not react.

[1] National Research Fellow in Chemistry.

[2] Aronheim, *Ann.*, **194**, 145 (1878); Hasenbaumer, *Ber.*, **31**, 2911 (1898); Goddard, *J. Chem. Soc.*, **121**, 40, 1161 (1922); Leicester and Bergstrom, THIS JOURNAL, **53**, 4428 (1931).

[3] Calingaert, *Chem. Reviews*, **2**, 73 (1925).

[4] Chambers and Scherer, THIS JOURNAL, **48**, 1056 (1926).

Experimental Part

Diphenyllead Dichloride and Diphenylmercury.—Four and five-tenths grams of diphenyllead dichloride and 3.5 g. of diphenylmercury in 75 cc. of pyridine were refluxed for ten hours. After cooling and filtering, the pyridine mother liquor was concentrated by distillation and then water was added to throw out the product. This was almost completely soluble in hot alcohol and on cooling gave 1.8 g. of crude phenylmercuric chloride which on recrystallization from alcohol melted at 250–252°. The product obtained on concentration of the alcohol mother liquor above was fractionated from alcohol or petroleum ether. One gram of triphenyllead chloride was obtained which after recrystallization from alcohol melted at 204–205°.

Di-*o*-tolyllead Dichloride and Diphenylmercury.—Di-*o*-tolyllead dichloride and diphenylmercury (4.6 g. and 3.5 g., respectively), in 200 cc. of alcohol were refluxed for six hours. The solution was concentrated and the reaction products separated by fractional crystallization first from alcohol and then from petroleum ether. There was obtained 1.2 g. of phenylmercuric chloride, m. p. 251–252°, and 0.5 g. of what was shown to be diphenyllead dichloride by halogen analysis and solubility behavior. Exhaustive fractionation of the remainder of the material failed to yield any other product which could be identified. The expected reaction product, phenyldi-*o*-tolyllead chloride, was prepared by a separate synthesis and its solubility and behavior on heating studied in order that it might not be overlooked.

Phenyldi-*o*-tolyllead Chloride.—This compound was prepared in a 70% yield from the bromide using the general procedure described for triphenyllead acetate.[5] It was recrystallized from ligroin or aqueous alcohol and melted at 113–114°.

Anal. Calcd. for $C_6H_5(C_7H_7)_2PbCl$: Pb, 41.29; Cl, 7.07. Found: Pb, 41.54; Cl, 6.77.

A small amount of the compound was refluxed in benzene and in alcohol for six hours and in each case it was recovered unchanged.

Disproportionation of Triphenyllead Chloride.—Five grams of triphenyllead chloride in 100 cc. of butyl alcohol was refluxed for six hours. Filtration gave 0.2 g. of an organic material which was undoubtedly diphenyllead dichloride. The solution on cooling gave 4 g. of product. Extraction with three 50-cc. portions of alcohol left 0.3 g. of tetraphenyllead which after recrystallization from benzene melted at 222–223°.

Disproportionation of Triethyllead Chloride.—Thirty-three grams of triethyllead chloride in 100 cc. of toluene was refluxed for five hours. Filtration gave 3 g. of insoluble material which was shown by analysis to be largely lead chloride. Most of the toluene was distilled and was replaced by petroleum ether. From this there was recovered 21.8 g. of triethyllead chloride and concentration of the filtrate gave 3.5 g. of an oil which was undoubtedly tetraethyllead. It was distilled under diminished pressure in an atmosphere of carbon dioxide and the index of refraction and density corresponded closely to the known values.

Tetraphenyllead and Diphenyllead Dichloride.—Five and one-tenth grams of tetraphenyllead and 4.3 g. of diphenyllead dichloride were dissolved and suspended in 250 cc. of butyl alcohol. The mixture was refluxed for eighteen hours and then filtered. The crude product obtained from the filtrate was recrystallized from alcohol and gave 8.1 g. of triphenyllead chloride, m. p. 202°.

Tetraethyllead and Diethyllead Dichloride.—Sixteen grams of tetraethyllead and 17 g. of diethyllead dichloride were dissolved and suspended in 100 cc. of benzene and refluxed for five hours. The mixture was filtered and most of the benzene was removed from the filtrate by distillation and was then replaced by petroleum ether.

[5] Austin, THIS JOURNAL, **53**, 3517 (1931).

The hot solution was clear and on cooling gave 13 g. of what was shown by halogen analysis and melting point to be triethyllead chloride.

The author is indebted to Professor C. S. Marvel for many helpful suggestions.

Summary

Diaryl lead dichlorides react in some cases with mercury diaryls to form the aryl mercuric chloride and a triaryl lead chloride.

Triaryl or alkyl lead halides disproportionate on heating to form a tetrasubstituted lead derivative and a disubstituted lead dihalide. Diaryl or alkyl lead dihalides react with their corresponding tetraaryl or alkyl derivatives to form trisubstituted lead halides in good yields.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SUBSTITUTION PRODUCTS OF ALPHA-NAPHTHOYL-ORTHO-BENZOIC ACID

BY E. H. JOHNSON,[1] V. WEINMAYR[2] AND ROGER ADAMS

RECEIVED MARCH 18, 1932 PUBLISHED AUGUST 5, 1932

The formation of anthraquinone and its substitution products through the condensation of phthalic anhydride with benzene and its derivatives has found wide commercial application. Among the variations of this general procedure certain substituted anthraquinones, otherwise difficult to obtain, can be prepared by substituting the intermediate benzoyl-*o*-benzoic acids and subsequently closing the ring to the anthraquinone.

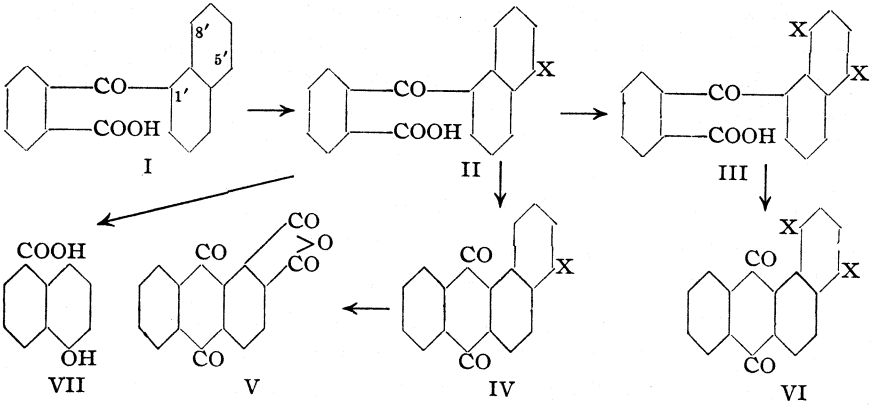
Benzanthraquinones have likewise been prepared from phthalic anhydride or substituted phthalic anhydrides with naphthalene or substituted naphthalenes,[3] though more difficulties are encountered so far as isomers are concerned than appear in the benzene series. The substitution of the intermediate α-naphthoyl-*o*-benzoic acids with subsequent conversion to the benzanthraquinones, however, has not been previously described. A number of such reactions are reported in this communication.

[1] This communication is an abstract of a thesis submitted by E. H. Johnson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Dr. V. Weinmayr, in the Laboratories of the Organic Chemicals Department, Dyestuffs Division of the du Pont Company, carried out the experiments on the chlorine derivatives.

[3] Ador and Crafts, *Bull. soc. chim.*, **34**, 531 (1880); Elbs *Ber.*, **19**, 2209 (1886); Gabriel, *ibid.*, **33**, 446 (1900); Scholl, *ibid.*, **44**, 2992 (1911); *ibid.*, **44**, 2370 (1911); *Monatsh.*, **32**, 997 (1911); **33**, 507 (1913); **41**, 583 (1920); Graebe, *Ann.*, **340**, 249 (1905); **340**, 259 (1905); Heller, *Ber.*, **41**, 3672 (1908); **45**, 665 (1912); Groggins, *Ind. Eng. Chem.*, **22**, 157 (1930); U. S. Patent 941,320 (1910); German Patent 234,917 (1911); Waldmann, *J. prakt. chem.*, **127**, 185 (1930); **127**, 201 (1930); Dziewonski, *Bull. Int. Acad. Pol.*, **3A**, 181 (1927); U. S. Patent 968,533.

α-Naphthoyl-o-benzoic acid (I) was readily chlorinated or brominated in glacial acetic acid either to a monochloro or monobromo (II) derivative. By further halogenation of the monohalogen products or by using two molecular equivalents of halogen with the α-naphthoyl-o-benzoic acid, dihalogen substitution products (III) resulted. With sulfuric acid as a solvent, the reaction proceeds rapidly toward the production of the dihalogen compound without stopping at the monohalogen state.

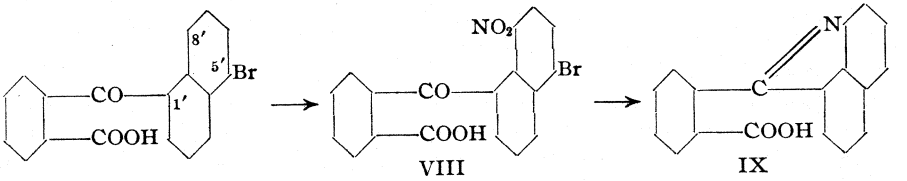


The position of the monosubstituted bromine compound was established. Upon oxidation with potassium permanganate of the bromo-1,2-benzanthraquinone (IV) obtained by ring closure of the bromo-α-naphthoyl-o-benzoic acid, anthraquinone-1,2-dicarboxylic acid anhydride (V) resulted which indicated that the bromine must be located in the original naphthalene nucleus. Its exact position was shown by fusing the bromo-α-naphthoyl-o-benzoic acid (II) with a mixture of sodium and potassium hydroxide at 200°. From the fusion 5-hydroxy-1-naphthoic acid (VII) was isolated and identified by its melting point and the melting point of its acetyl derivative, thus showing the original compound to be 5′-bromo-1′-naphthoyl-2-benzoic acid. It is fair to assume that the chlorine occupies the same position. The positions 5′, 8′ might be expected for the dihalogen compounds and by analogy to the structure of the nitro compounds discussed below these positions appear reasonably certain.

The monochloro- or bromo-1′-naphthoyl-2-benzoic acids were readily converted to the corresponding benzanthraquinones (IV) by means of sulfuric acid with or without boric acid. The dihalogen compounds were, in a similar manner, converted to benzanthraquinones (VI). A single dibromobenzanthraquinone was isolated, but from the dichloronaphthoylbenzoic acid, two isomeric dichlorobenzanthraquinones were obtained. It would appear that during the dehydration, migration of the halogens must have occurred to some extent. As a consequence, the exact structure of these dihalogen benzanthraquinones is not certain. It is probable,

however, that the dibromo and one of the dichloro compounds are 5′, 8′ disubstitution products.

The chloro- and bromo-1′-naphthoyl-2-benzoic acids were nitrated to mononitro derivatives (VIII). The 8′-position for this nitro group might be anticipated and subsequent experiments showed this to be the case Upon reduction, the nitrobromo-1′-naphthoyl-2-benzoic acid gave a product, not an amine but obviously a secondary product (IX) acid in character with water eliminated. This could have formed only if the nitro were in the 8′ position. This is a product analogous to that reported by



VIII IX

Scholl and Wolodkowitsch[4] upon reduction of bz-1-nitro-1,2-benzanthraquinone.

The 5′-bromo-1′-naphthoyl-2-benzoic acid may also be nitrated in acetic anhydride. Under these conditions the product proved to be a dinitro-α-naphthoyl-*o*-benzoic acid. Bromine had been eliminated completely. It seems probable that the first nitro group was introduced in the 8′-position as in the mononitro monobromo compound, and since the bromine is eliminated, it is a natural conclusion that the second nitro has probably taken its place, leading to 5′,8′-dinitro-1′-naphthoyl-2-benzoic acid.

Experimental

α-Naphthoyl-*o*-benzoic Acid.—This product was made by the procedure of Heller and Schulke[5] as modified by Groggins and Newton.[6] The only modification which was followed was in the purification. It was found that, in the laboratory at least, it could be crystallized readily from a large volume of toluene and purified much more readily than through the ammonium salt as previously recommended. The crude material obtained by following directions specified gave a product melting at 153–165° which, upon two recrystallizations from toluene gave a melting point of 173–173.5°. By evaporating the toluene mother liquors from the crystallizations there was no difficulty in recovering essentially all of the α-naphthoyl-*o*-benzoic acid present.

5′-Bromo-1′-naphthoyl-2-benzoic Acid (II).—To 100 g. of α-naphthoyl-*o*-benzoic acid in a 500-cc., round-bottomed flask fitted with a glass-jointed reflux condenser, were added 100 cc. of glacial acetic acid and 36 cc. (115 g.) of bromine and the mixture was refluxed for four hours. The reaction mixture was then cooled in an ice–salt bath until it had all solidified. On warming the flask to room temperature, a precipitate of 5′-bromo-1′-naphthoyl-2-benzoic acid was present. This was filtered out and dried; yield, 89.2 g. (69.5%). The compound was purified by two recrystallizations from toluene, m. p. 203–204°.

[4] Scholl and Wolodkowitsch, *Ber.*, **44**, 2370 (1911).

[5] Heller and Schulke, *ibid.*, **41**, 3670 (1908).

[6] Groggins and Newton, *Ind. Eng. Chem.*, **22**, 157 (1930).

Anal. Calcd. for $C_{18}H_{11}O_3Br$: neut. equiv., 355; Br, 22.51. Found: neut. equiv., 350; Br, 22.35.

5',8'-Dibromo-1'-naphthoyl-2-benzoic Acid.—In a mortar 5 g. of pure α-naphthoyl-*o*-benzoic acid was ground with a trace of ferric chloride and a trace of iron powder and placed in a 125-cc. Erlenmeyer flask. Five cc. of bromine was allowed to drop slowly onto this mixture. After the bromine was all added, the reaction mixture was allowed to stand for three to four hours at room temperature and was then treated with dilute sodium hydroxide solution. All of the product dissolved in the boiling solution leaving a residue of ferric hydroxide. This was filtered off and on cooling a small amount of the sodium salt precipitated. The solution was acidified with dilute hydrochloric acid and a white precipitate was produced; yield, 4.5 g. (57.3%). The dibromo compound was purified by crystallization from toluene or glacial acetic acid. It formed fine white needles, m. p. 260–261°.

Anal. Calcd. for $C_{18}H_{10}O_3Br_2$: Br, 36.84. Found: Br, 36.72.

An alternate procedure is to dissolve 276 g. of α-naphthoyl-*o*-benzoic acid in 1370 g. of 93% sulfuric acid at 50°, and to add 160 g. of bromine slowly at this temperature, which is maintained for twenty-two hours longer. The temperature is then raised slowly to 70° to complete the reaction. The mass is now poured into 4 liters of ice water and the yellow precipitate is filtered and washed. The cake is extracted with dilute sodium hydroxide (to separate it from a considerable amount of ring-closed product) and the clear solution is run into ice and acid. The product is purified as described above and melts at 260–261°. The mixed melting point of the products made by the two methods was unchanged.

Anal. Calcd. for $C_{18}H_{10}O_3Br_2$: Br, 36.84. Found: Br, 36.68.

Proof of the Position of Bromine Atom in Bromo-α-naphthoyl-*o*-benzoic Acid

1. Oxidation[7] of the Benzanthraquinone from Bromo-α-naphthoyl-*o*-benzoic Acid.—A solution of 10 g. of monobromobenzanthraquinone in 160 g. of concentrated sulfuric acid was poured into 400 cc. of water so that the product was precipitated in a finely divided form. This suspension was then heated to boiling and 75 g. of potassium permanganate was added in small portions. This was followed by solid oxalic acid until the black color was entirely gone. The hot solution was filtered, leaving a light yellow residue on the filter paper. More of this light colored solid precipitated when the hot filtrate had cooled. The precipitate from the hot filtration was treated with dilute aqueous ammonia, filtered, then acidified, when fine needles precipitated. This precipitate was then united with the one obtained from the cooling of the original oxidation solution and recrystallized twice from acetic anhydride (V). Light yellow needles were formed, m. p. 322–324°. This substance was shown to be anthraquinone-1,2-dicarboxylic acid anhydride by comparing it with an authentic sample prepared by oxidation of 1,2-benzanthraquinone.[7]

2. 5-Hydroxy-1-naphthoic Acid by Fusion of Monobromo-α-naphthoyl-*o*-benzoic Acid with Potassium Hydroxide.—A mixture of 100 g. of sodium hydroxide, 100 g. of potassium hydroxide, and 25 g. of potassium nitrate was placed in a 500-cc., two-necked flask and heated until melting took place. A stirrer and condenser were placed in the center neck while a thermometer was placed in the side-neck. The stirrer was started and the flask was cooled to 200°. This temperature was maintained throughout the reaction. With continuous stirring 10 g. of bromo-α-naphthoyl-*o*-benzoic acid was added in small portions. When all had been added, the reaction mixture was stirred for fifteen minutes longer and then allowed to cool. The melt was dissolved in

[7] General Method of Scholl and Schwinger, *Ber.*, **44**, 2992 (1911); Scholl and Graz, German Patent 241,624.

water and poured into a large volume of iced dilute hydrochloric acid. This solution was then extracted with ether. The ether extract was evaporated to a small volume and poured into a large volume of petroleum ether. A reddish-purple tar was precipitated. The liquid was decanted after standing, during which more tar appeared, was decanted again and then evaporated to dryness. The yellow residue thus obtained was dissolved in boiling water and treated with norite for a few minutes. The solution was filtered while hot and on cooling a white precipitate appeared. This was recrystallized twice from water to a constant m. p. of 236–237°. This is the melting point given in the literature for 5-hydroxy-1-naphthoic acid (VII).[8]

Some of this precipitate was then refluxed for two hours with acetic anhydride. The acetic anhydride was distilled off under reduced pressure and the resulting residue was recrystallized three times from water. It was a white solid, m. p. 198–201°. This is the melting point of the acetyl derivative of 5-hydroxy-1-naphthoic acid.[8]

5′-Chloro-1′-naphthoyl-2-benzoic Acid.—A solution of 414 g. of α-naphthoyl-*o*-benzoic acid in 500 g. of glacial acetic acid was treated at 114–118° with chlorine gas until it increased in weight by about 53 g. The red solution was poured onto a large amount of ice and water and the precipitate filtered. It weighed 440 g. (94.4%). White crystals, m. p. 179–180°, formed after purification from toluene.

Anal. Calcd. for $C_{18}H_{11}O_3Cl$: Cl, 11.42. Found: Cl, 11.35.

5′,8′-Dichloro-1′-naphthoyl-2-benzoic Acid.—Into a solution of 276 g. of α-naphthoyl-*o*-benzoic acid in 1370 g. of 93% sulfuric acid at 30–70°, chlorine was passed until it had gained 87 g. in weight. The solution was then poured onto ice and water. The filtered mass was extracted with hot dilute sodium hydroxide, which left about 92 g. of chlorinated benzanthraquinones. The alkaline solution was acidified and the product recrystallized from glacial acetic acid. White crystals of 5′,8′-dichloro-1′-naphthoyl-2-benzoic acid, m. p. 242°, were obtained.

Anal. Calcd. for $C_{18}H_{10}O_3Cl_2$: Cl, 20.60. Found: Cl, 20.54.

The chlorination in glacial acetic acid gives the same dichloro compound as the chlorination in sulfuric acid but in much poorer yields.

Halogenated 1,2-Benzanthraquinones

Bz-4-bromo-1,2-benzanthraquinone (IV).—A solution of 20 g. of 5′-bromo-1′-naphthoyl-2-benzoic acid in 400 cc. of concentrated sulfuric acid was heated for exactly fifteen minutes at 115–117° and then was poured into a large volume of ice and water. The total reaction time was twenty minutes. A yellow precipitate was produced which was filtered off and treated with dilute sodium hydroxide solution to dissolve any unreacted material. The product was recrystallized from glacial acetic acid and gave greenish-yellow bulky needles, m. p. 231–232°; yield, 10.8 g.

Anal. Calcd. for $C_{18}H_9O_2Br$: Br, 23.71. Found: Br, 23.08, 23.39.

Bz-1,4-dibromo-1,2-benzanthraquinone (VI).—A solution of 4.8 g. of 5′,8′-dibromo-1′-naphthoyl-2-benzoic acid in 30 cc. of concentrated sulfuric acid was heated at 122–124°, with or without 3 g. of boric acid, for twenty minutes. The sulfuric acid solution was immediately poured into a large volume of ice and water. A yellow precipitate was produced. This was filtered out, washed several times with water and then heated to the boiling point in 1300 cc. of dilute sodium hydroxide solution. Most of the yellow precipitate did not dissolve and after the solution cooled, it was filtered off; yield, 2.5 g. (54.3%). The product was purified by crystallization from benzene and gave a bright yellow solid, m. p. 265–266°.

Anal. Calcd. for $C_{18}H_8O_2Br_2$: Br, 38.44. Found: Br, 38.16.

[8] Royle and Schedler, *J. Chem. Soc.*, **123**, 1647 (1923).

Bz-4-chloro-1,2-benzanthraquinone.—A solution of 45 g. of 5′-chloro-1′-naphthoyl-2-benzoic acid in 450 g. of 100% sulfuric acid containing 45 g. of boric acid was heated to 115–120° and held for twenty minutes. The ring-closed mass was poured onto a large amount of ice and water. The yellow precipitate was filtered, washed and extracted with hot dilute caustic solution. The yield was 38 g. (90.5%). Upon crystallization from glacial acetic acid, bright yellow needles were formed which melted at 232°.

Anal. Calcd. for $C_{18}H_9OCl$: Cl, 12.13. Found: Cl, 12.10.

Bz-dichloro-1,2-benzanthraquinones.—Seventy grams of 5′,8′-dichloro-1′-naphthoyl-2-benzoic acid melting at 242° was added to a solution of 70 g. of boric acid in 700 g. of 100% sulfuric acid, heated to 160° and held for thirty minutes at 160–165°. The solution was cooled quickly to 100°, then poured onto a large amount of ice and water. The yellow precipitate was filtered, washed and extracted with hot dilute caustic solution. The yield was 30 g. (45.2%) of product melting at 240–300°.

Twenty-eight grams of the dry ring-closed product was extracted twice with 80 cc. of hot chlorobenzene. On cooling the extract, fine yellow needles separated which were filtered and recrystallized from 100 cc. of toluene. The fraction (7 g.) melted at 237–238°.

Anal. Calcd. for $C_{18}H_8O_2Cl_2$; Cl, 21.70. Found: Cl, 21.47.

The residue insoluble in chlorobenzene was further extracted hot with 380 cc. of chlorobenzene and 55 cc. of nitrobenzene. The precipitate from these extractions was filtered and recrystallized from 250 cc. of chlorobenzene. Five grams of dark yellow needles was obtained melting at 304°.

Anal. Calcd. for $C_{18}H_8O_2Cl_2$: Cl, 21.70. Found: Cl, 21.57.

8′-Nitro-5′-bromo-1′-naphthoyl-2-benzoic Acid. (VII.)—A solution of 97 g. of 5′-bromo-1′-naphthoyl-2-benzoic acid in 550 g. of 100% sulfuric acid was cooled to 10° and nitrated under agitation with 90 g. of a mixed acid containing 21% nitric acid and 69% sulfuric acid at 5–10°. After stirring for an hour, a test showed no nitric acid. Upon dilution with water the nitro compound precipitated (yield, 112 g.). It was purified by crystallization from hot nitrobenzene or *n*-butyl alcohol. The product consisted of white crystals, m. p. 228–230°.

Anal. Calcd. for $C_{18}H_{10}O_5NBr$: Br, 19.97; N, 3.50. Found: Br, 19.98; N, 3.51.

Reduction of 8′-Nitro-5′-bromo-1′-naphthoyl-2-benzoic Acid.—A solution of 4 g. of 8′-nitro-5′-bromo-1′-naphthoyl-2-benzoic acid in 100 cc. of acetic anhydride was reduced with 0.05 g. of platinum-oxide platinum black at 2.5 atm. pressure and a temperature of 80°. The catalyst was filtered and the acetic anhydride was distilled off under reduced pressure. A deep red tar remained in the flask which was washed with ether several times. An oil apparently dissolved in the ether leaving a brown solid. The solid was recrystallized twice from *n*-butyl alcohol to give a light brown amorphous product. It had no melting point, but merely turned black gradually.

Anal. Calcd. for $C_{18}H_{10}O_2NBr$: Br, 22.70. Found: Br, 22.18.

The same product is formed if iron and acid are used as a reducing agent.

8′-Nitro-5′-chloro-1′-naphthoyl-2-benzoic Acid.—A solution of 109 g. of 5′-chloro-1′-naphthoyl-2-benzoic acid in 600 g. of 100% sulfuric acid at 20–25° was cooled to 0–5° and nitrated with 110 g. of nitrating mixture containing 20% nitric acid and 69% sulfuric acid. The product was poured into water and ice; yield, 130 g. The compound is readily purified from chlorobenzene, m. p. 233–234°.

Anal. Calcd. for $C_{18}H_{10}O_5NCl$: Cl, 10.0; N, 3.94. Found: Cl, 10.78; N, 3.74.

5′,8′-Dinitro-1′-naphthoyl-2-benzoic Acid.—Into a solution of 30 g. of 5′-bromo-1′-naphthoyl-2-benzoic acid in 160 cc. of acetic anhydride was dropped slowly with stirring 30 cc. of concentrated nitric acid. The temperature of the reaction was not allowed to go above 30°. The solution was stirred for eight hours after the nitric acid

had all been added, during which time an appreciable quantity of the yellow 5′,8′-dinitro-1′-naphthoyl-2-benzoic acid precipitated and was filtered. The acetic anhydride filtrate was poured into a large volume of water and allowed to stand overnight to decompose the acetic anhydride. A yellow precipitate was produced which was filtered and dried at room temperature. The precipitate was then crystallized twice from boiling toluene; yield, 10 g. (32%) of yellow plates. If heated rapidly it melted sharply at 262–263° (decomp.).

Anal. Calcd. for $C_{18}H_{10}O_7N_2$: C, 59.0; H, 2.43. Found: C, 59.9; H, 2.52.

Summary

1. A study of the substitution of α-naphthoyl-*o*-benzoic acid has been made. By the action of chlorine or bromine, either the 5′- or 5′,8′-disubstitution derivatives are obtained which may readily be dehydrated to the corresponding benzanthraquinones.

2. Proof of the 5′-position of the monobromo derivative was established by oxidation of the bromobenzanthraquinone to anthraquinone-1,2-dicarboxylic acid and by fusion of the bromo-α-naphthoyl-*o*-benzoic acid with sodium and potassium hydroxide to yield 1-hydroxy-5-naphthoic acid.

3. Nitration of 5′-chloro- or bromo-1′-naphthoyl-2-benzoic acid gave the 8′-nitro derivative, as shown by the fact that on reduction a ring structure was produced characteristic of 1-keto-8-aminonaphthalenes. Further nitration gave a halogen-free dinitro compound, probably 5′,8′-dinitro-1′-naphthoyl-2-benzoic acid.

URBANA, ILLINOIS

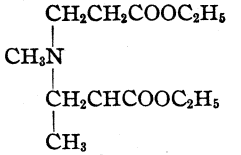
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE DEAMINATION OF ETHYL BETA-METHYLAMINOPROPIONATE

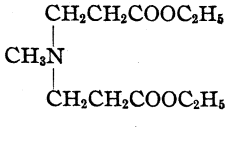
BY W. B. THOMAS AND S. M. MCELVAIN

RECEIVED MARCH 22, 1932 PUBLISHED AUGUST 5, 1932

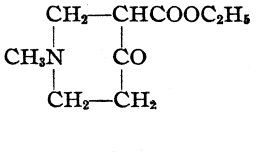
In an attempt to prepare β-carbethoxyethyl-β-carbethoxypropylmethylamine (I), ethyl β-methylaminopropionate was treated with ethyl β-bromoisobutyrate. Instead of the desired compound the product which was obtained was β,β′-dicarbethoxydiethylmethylamine[1] (II) as shown by the fact that it was converted by sodium ethoxide into 1-methyl-3-carbethoxy-4-piperidone[1] (III).



I



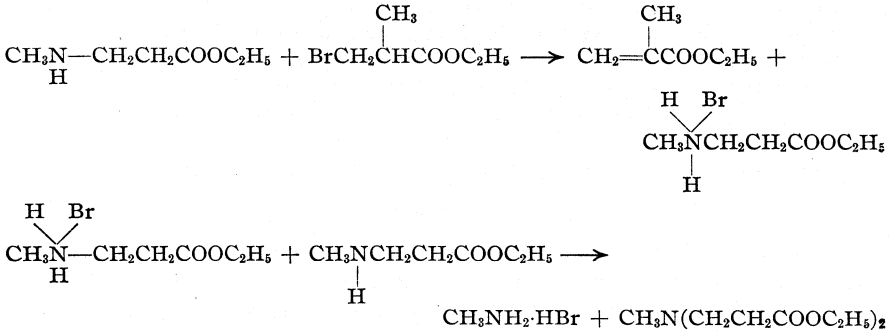
II



III

[1] McElvain, THIS JOURNAL, **46**, 1721 (1924).

The course which the reaction had taken may be shown, thus



Since ethyl β-methylaminopropionate readily adds to ethyl acrylate to give the amino ester (II) it is probable that ethyl acrylate is an intermediate in the second phase of the above reactions. For this reason it seemed likely that the unsymmetrical amino ester (I) might be obtained by the addition of ethyl β-methylaminopropionate to ethyl α-methylacrylate. However, this reaction also yielded the symmetrical amino ester (II). It is evident, therefore, that ethyl β-methylaminopropionate as well as its salt readily loses methylamine to form a tertiary amino ester, thus



Since it is probable that this reaction also involves the intermediate formation of ethyl acrylate[2] it is quite surprising that both the formation of this latter ester and the addition of a molecule of the secondary amino ester to it take place rather than the addition of any appreciable amount of the secondary amino ester to the ethyl α-methylacrylate.

Experimental

Ethyl β-Bromoisobutyrate.—This ester was prepared by the addition of hydrogen bromide to α-methyl acrylate.[3] The yield of ethyl α-methyl-β-bromopropionate was 76% of the theoretical, b. p. 68–72° (14 mm.), n_D^{25} 1.44506, d_{25}^{25} 1.3275. This ester distils with slight decomposition at 180–180.5° at atmospheric pressure. Calcd. for $C_6H_{11}O_2Br$, Br: 40.96. Found: 41.12. Recently Vocke[4] obtained methyl β-bromoisobutyrate by the action of hydrogen bromide on a methyl alcoholic solution of α-methylacrylic acid.

Ethyl β-Methylaminopropionate from Ethyl β-Benzoylmethylaminopropionate.—To a solution of 48 g. of ethyl β-methylaminopropionate[5] in 30 cc. of acetone was added 100 g. of anhydrous potassium carbonate. Then, during vigorous stirring, 66 g. of

[2] *Cf.* Abderhalden, *Z. physiol. Chem.*, **85**, 114 (1913); Fuson, THIS JOURNAL, **50**, 1448 (1928).

[3] Ruzicka, *Helv. Chim. Acta*, **2**, 152 (1919).

[4] Vocke, *Z. physiol. Chem.*, **191**, 83 (1930).

[5] McElvain, THIS JOURNAL, **46**, 1726 (1924).

benzoyl chloride was added from a dropping funnel at such a rate that the acetone did not reflux too vigorously. After this addition the acetone was refluxed and stirred for ten hours. The solid precipitate was then filtered off and the acetone removed by distillation. The residue was taken up in ether, washed with dilute hydrochloric acid and dilute sodium hydroxide and, after drying over anhydrous potassium carbonate, distilled. The yield of the benzoyl derivative was 86 g. (62%); b. p. 155–157° (3 mm.); n_D^{25} 1.51741; d_{25}^{25} 1.1076. Calcd. for $C_{13}H_{17}O_3N$: N, 5.96. Found: N, 6.31.

This benzoyl derivative was hydrolyzed by refluxing for eight hours with 20% hydrochloric acid. After cooling the precipitated benzoic acid was filtered off and any remaining in solution extracted with ether. The acid solution was evaporated to dryness and the residue esterified as previously described.[5] The yield of ethyl β-methylaminopropionate from 48 g. of the benzoyl derivative was 18 g. (67%). It boiled at 60.5–61° (10 mm.); n_D^{25} 1.41990; d_{25}^{25} 0.9502. Calcd. for $C_6H_{13}O_2N$: N, 10.7. Found: N, 11.1. The secondary amino ester obtained by the above procedure differs quite materially in physical properties from the product previously described.[5]

Reaction of Ethyl β-Methylaminopropionate and Ethyl β-Bromoisobutyrate.—A mixture of 70.1 g. (2 mols) of ethyl β-methylaminopropionate and 52.2 g. (1 mol) of ethyl β-bromoisobutyrate was heated in an oil-bath at 130–140° for two hours. After this time the reaction mixture was cooled, diluted with ether and the ethereal solution separated by decantation from the semi-crystalline precipitate. From an alkaline solution of this precipitate methylamine was distilled out and characterized as methyl benzamide, m. p. 79–80°. After removal of the ether from the ethereal extract the residue was fractionated and the following fractions collected: (1) 9.5 g. below 50° (25 mm.), (2) 8.9 g. at 40–50° (4 mm.) and (3) 37.5 g. at 116–117° (4 mm.). Fraction (1) was mainly ethyl α-methylacrylate, (2) unchanged secondary amine and (3) was a tertiary amino ester which gave 6.25% N on analysis. (Calcd. for symmetrical ester (II), 6.06% and unsymmetrical ester (I), 5.72%.) This tertiary amino ester was condensed by sodium ethoxide to 1-methyl-3-carbethoxy-4-piperidone (III).

Reaction of Ethyl β-Methylaminopropionate with Ethyl α-Methylacrylate.—A mixture of 12.4 g. (1 mol) of the secondary amino ester and 10.8 g. (1 mol) of the unsaturated ester was heated in an oil-bath at 130–140° for three hours. After this time the reaction mixture was fractionated and the following fractions obtained (1) 8.9 g. of ethyl α-methylacrylate, (2) 4.9 g. of secondary amino ester and (3) 6 g. of a tertiary amino ester. A residue of polymerized methylacrylate remained. Fraction (3) was shown to be the β,β′-dicarbethoxydiethylmethylamine (II) by analysis (found, 6.12 N) and by the fact that sodium ethoxide condensed it to 1-methyl-3-carbethoxy-4-piperidone as above.

Preparation of β,β′-Dicarbethoxydiethylmethylamine (I) from Ethyl β-Methylaminopropionate.—(1) To 8.4 g. (1 mol) of the secondary amino ester was added 13.5 g. (1 mol) of its hydrobromide and the mixture heated in an oil-bath at 130–140° for three hours. After cooling, ether was added and the ethereal solution decanted from the precipitated hydrobromide. On distillation of the ethereal extract, 1.5 g. of unreacted secondary amino ester and 5 g. (34%) of the tertiary amino ester (II) was obtained. To the hydrobromide residue left after the ether decantation 30 cc. of 20% sodium hydroxide was added. Then about half of the alkaline solution was carefully distilled into standard acid and the methylamine determined; 0.99 g. (51%) was found.

(2) A 25-g. sample of the secondary amino ester when heated under a reflux condenser at 130–140° for four hours evolved 0.445 g. (14.8%) of methylamine. Fractionation of the remaining ester yielded 18.9 g. of unchanged secondary amino ester and 3.4 g. (15%) of the tertiary amine (II).

(3) A mixture of 7 g. of ethyl acrylate and 9.2 g. of the secondary amino ester

was heated under reflux in an oil-bath at 110–120° for two hours. Distillation of the reaction mixture yielded small amounts of unreacted acrylic and secondary amino esters and 11.6 g. (80%) of tertiary amino ester (II).

Summary

It has been found that when ethyl β-methylaminopropionate is allowed to react with either ethyl β-bromoisobutyrate or ethyl α-methylacrylate the product obtained is not the expected β-carbethoxyethyl-β-carbethoxypropylmethylamine, but is β,β′-dicarbethoxyethylmethylamine which is formed by the elimination of methyl amine (or its salt) from two molecules of the secondary amino ester.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

RYE GERM OIL

BY ALBERT W. STOUT AND H. A. SCHUETTE

RECEIVED MARCH 25, 1932 PUBLISHED AUGUST 5, 1932

Little published information[1] on the composition of the oil in rye, *Secale cerealae* L., is available. That which has found its way into the literature is of European origin and is not pertinent to the same type of product in each instance inasmuch as the whole kernel,[1a,d,h] its bran,[1b] its embryo[1g] and its flour[1c,h] and breads[1h] baked therefrom have been used as the sources of the oil or "ether extract," under examination. The inevitable result of this diversity in selection of raw material has been a lack of correlation of data.[2] Furthermore, with one exception,[1h] all of the reports in question are incomplete when viewed in the light of the newer trends in the technique of fatty oil analysis.

Unlike the embryo oils of other cereals such as corn and wheat, rye oil finds at present no important technical or alimentary use. The facts that it is apparently rich in the carotinoid pigments, that it contains a high percentage of lecithin-bearing unsaponifiable matter, and that the antimony trichloride test which is presumed to be indicative of the presence of vitamin A is positive, suggest the thought that the clinical advantages of

[1] (a) König, *Landw. Vers. Sta.*, **17**, 1 (1874); (b) Stellwaag, *ibid.*, **37**, 135 (1890); (c) Spaeth, *Forschungsber. Lebensm.*, **3**, 251 (1896), through *Z. Nahr. Genussm.*, **11**, 410 (1896); (d) Meyer, *Chem.-Ztg.*, **27**, 958 (1903); (e) Grimme, *Seifensieder-Ztg.*, **45**, 704 (1918); (f) Herbig, *Seifenfabrikant*, **38**, 497 (1918); (g) Alpers, *Chem.-Ztg.*, **42**, 37 (1918); (h) Croxford, *Analyst*, **55**, 735 (1930).

[2] This is particularly noticeable in the description of the color—it has been variously reported as being dark green to yellowish-brown—and other external characteristics of the oil and in the records of its simpler chemical constants. Iodine numbers, for example, have been reported as lying between 81.8 and 127.7; saponification numbers between 172.8 and 196.0; and the content of unsaponifiable matter to vary between 8.2 and 11.20%.

the presence of rye oil in the diet might profitably be investigated. There are, however, obvious needs both for a definition of the term rye oil and a better knowledge of the chemistry of the lipin which is elaborated in the embryo or germ of the kernel. Precedent and consistency, it seems, dictate that, apart from all the substances recoverable by solvent extraction from this cereal grain and its products, the term rye oil should be reserved for the constituent in question in the embryo.

A re-investigation of this oil appears then justified in view of the unsatisfactory state of our knowledge of its chemistry and the fact that no record appears to be extant on a domestic product which had been recovered exclusively from the embryo. A report of such a study is made the subject of this communication.

I. Preparation of Material

The oil in question was obtained by extracting with sulfur-free petroleum ether (b. p. 30–60°) rye embryo (oil content 11%) recovered by repeated sifting and air cleaning of so-called rye germ stock,[3] a by-product in the milling of the grain. The last traces of solvent were removed by distillation at reduced pressures on a water-bath and in the presence of carbon dioxide. The oil was found to be of a deep golden-brown color. It possesses an odor suggestive of the grain itself and, in contradistinction to the report that rye oil is of a semi-solid consistency at 15°,[1h] was found still to be plastic at −60°.

II. Analysis of the Oil

(a) **Chemical and Physical Characteristics.**—The important chemical and physical constants (Table I) were determined by recognized procedures.[4] In the determination of the thiocyanogen number of the fatty acids and the interpretation of this constant the procedure of Kaufmann was followed.[5] Because of the presence of the relatively large quantities of unsaponifiable matter, this was first removed before the acids were subjected to analysis. Separation of the fatty acids into saturated and unsaturated groups was effected by the lead salt–ether[6a] method, after which corrections were made for the small amount of unsaturated acids contaminating the former, when this procedure is used,[6b] and for the unsaponifiable matter accompanying the insoluble acids.

[3] Acknowledgment is made to the Messrs. Frank H. Blodgett, Inc., of Janesville, Wisconsin, who by gratuitously placing at our disposal some two hundred pounds of this material, made possible this investigation.

[4] Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 1930, 3d ed., pp. 314–330.

[5] Kaufmann, *Z. nahr. Genussm.*, **51**, 15 (1926); "Deutsche Einheitsmethoden," 1930, Wizoff, Stuttgart, 1930, pp. 94–97.

[6] (a) Gusserow, *Arch. Apoth.-Vereins nord. Teutschland*, **27**, 153 (1828); Varrentrapp, *Ann.*, **35**, 196 (1840); (b) Jamieson, *J. Assoc. Official Agri. Chem.*, **11**, 303 (1928).

TABLE I

CHEMICAL AND PHYSICAL CHARACTERISTICS OF RYE GERM OIL

Specific gravity 20/20°	0.9229
Index of refraction, 20°	1.4779
Titer test, °C.	25.2
Iodine number[a] (Wijs)	139.91
Saponification number	176.81
Reichert–Meissl number	0.05
Polenske number	.3
Free fatty acids (per cent. oleic)	2.9
Acetyl number	20.19
Soluble acids (per cent. as butyric)	trace
Insoluble acids (Hehner number)[b]	84.45
Iodine number (Wijs) of insoluble fatty acids[b]	133.57
Thiocyanogen number of insoluble fatty acids[b]	85.05
Unsaturated acids (per cent.) corrected	77.46
Saturated fatty acids (per cent.) corrected	10.12
Iodine number of unsaturated acids (Wijs)	158.90
Saponification number of unsaturated acids	172.6
Unsaponifiable matter (per cent.)	7.28

[a] The iodine number when determined by the Hanus method was found to be 134.0. This figure represents an average of four determinations. [b] Corrected for unsaponifiable matter.

(b) Unsaturated Acids.—Separation of the unsaturated acids was effected through the preparation of their bromo addition compounds and the fractional separation of the mixture into its components by the use, in turn, of diethyl and petroleum ethers.[7] The presence of linolenic acid was indicated by the formation of an ethyl ether-insoluble precipitate in the cold (−10°). Analysis proved the latter to be the hexabromide of this acid. A considerable quantity of the tetrabromo derivative of linoleic acid (Br, 53.62%) separated from the cold petroleum ether solution. The bromine content (43.43%) of the dibromide fraction showed it to be a mixture of this compound and the tetrabromo derivative. Using the latter value and those expressing the bromine content of the oleic and linoleic derivatives, respectively, the percentage composition of the mixture was calculated.[8]

The composition of this fraction was also arrived at, and perhaps with greater accuracy of results since gravimetric separations are not involved, by the mode of procedure suggested by Kaufmann,[5] a scheme of analysis in which the iodine (133.57) and thiocyanogen (85.05) numbers of the purified fatty acids become the point of departure in a mathematical calculation. Exact agreement was not obtained by these two different methods of approach, yet the order of magnitude of the quantities of each acid present is substantially the same (Table II).

[7] Eibener and Muggenthaler, *Farben-Ztg.*, **18**, 131 (1912).

[8] Baughman and Jamieson, THIS JOURNAL, **42**, 157 (1920).

TABLE II

PERCENTAGE COMPOSITION OF THE UNSATURATED ACID FRACTION

Acid	In oil		Glycerides in oil	
	Obs.[a]	Calcd.[b]	Obs.[a]	Calcd.[b]
Oleic	36.17	30.54	37.79	31.92
Linoleic	38.92	42.14	40.68	44.05
Linolenic	2.37	4.78	2.48	4.99

[a] From bromine addition products. [b] From thiocyanogen number.

(c) **Saturated Acids.**—The methyl esters of the saturated acids were separated into five fractions (Table III) of boiling range 163 to 181° (5 mm). The average molecular weights of the respective fractions as calculated from saponification and iodine numbers—the latter serving as a basis for correcting each for the presence of unsaturated acids—indicated the presence of acids in the C_{14} to C_{18} group.

TABLE III

RESULTS OF ANALYSES OF METHYL ESTERS OF THE SATURATED FATTY ACIDS

Fraction	Wt., g.	Iodine no.	Sapon. no.	Mean mol. wt.	Myristic ester	Palmitic ester	Stearic ester
1	7.30	2.76	215.6	257.6	3.203	3.894	...
2	9.72	3.37	211.2	265.0	1.745	7.759	...
3	15.68	7.56	209.5	266.4	2.024	11.876	...
4	2.30	22.59	209.3	263.8	0.450	1.507	...
5	1.01	43.25	196.5	270.7	...	0.686	...
Res.	3.35					.432	0.598
Total					7.422	26.154	.598

These data lead to the following statement of the percentage composition of the saturated acid fraction.

TABLE IV

PERCENTAGE COMPOSITION OF THE SATURATED ACID FRACTION

Acid	Myristic	Palmitic	Stearic
In oil	2.21	7.73	0.17
Glycerides in oil	2.33	8.11	.18

(d) **Miscellaneous.**—The phosphorus content of both the oil itself and its unsaponifiable matter was determined in the usual manner after the organic matter, saturated with sodium hydroxide solution, had been destroyed by incinerating it. From the data so obtained the lecithin equivalent of a hypothetical di-oleyl derivative ($C_{44}H_{86}O_9NP$) was calculated. It was found to be 1.33% for the oil and 3.05% for its unsaponifiable matter. The former value is somewhat higher than the lecithin content (1.04%) of a purified rye oil reported by Alpers[1g] but less than that found by him (3.04%) in a crude oil. It compares very favorably with the lecithin content of a corn oil (1.49%) examined by Hopkins[9] but is

[9] Hopkins, THIS JOURNAL, **20**, 948 (1898).

lower than that found in wheat germ oil (2.00%) by Frankforter and Harding.[10]

The deep golden-brown color of this oil suggests the presence of the carotinoid pigments. In view of the fact that vitamin A potency is now generally associated with carotene, and since the antimony chloride reaction[11] is presumed to indicate its presence, application of this test bid fair to lead to affirmative results.

When the oil itself was added to a chloroform solution of this salt, a strong blue coloration appeared. The unsaponifiable matter which had been extracted with ethyl ether gave a stronger reaction than did that recovered by treatment with petroleum ether, a condition which is probably due to the fact that the latter removes less coloring matter from the oil than does the former.

Summary

The more important physical and chemical characteristics and the approximate percentage composition of rye germ oil have been determined. It is a semi-drying oil which is characterized by the quantity of heavily pigmented unsaponifiable matter which it contains. Correlation of its constants with those obtained by others, with perhaps one exception,[1g] cannot satisfactorily be made because of the diversity of products which have been included under the name rye oil.

The percentage composition of this oil was found to be as follows: myristin, 2.33; palmitin, 8.11; stearin, 0.18; olein, 31.92; linolein, 44.05; linolenein, 4.99; unsaponifiable matter, 7.28; undetermined, 1.14.

[10] Frankforter and Harding, THIS JOURNAL, **21**, 758 (1899).

[11] Carr and Price, *Biochem. J.*, **20**, 497 (1926).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. VIII. FURTHER DETERMINATIONS OF STRUCTURES. QUESTION OF ISOMERS

BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED MARCH 26, 1932 PUBLISHED AUGUST 5, 1932

The present paper deals mainly with the determination of the structure of a number of mixed benzoins, most of them new, in continuation of the authors' purpose to characterize a sufficiently large number of mixed benzoins to enable worth-while deductions to be made regarding the reactivity of aldehydes. The method used depends on the Beckmann transformation of the second type, previously used and described in Part IV.[1] The reaction appears to be trustworthy, as no results so far obtained contradict

[1] Buck and Ide, THIS JOURNAL, **53**, 1912 (1931).

structures established in other ways. The transformation is considered as taking place in the Beckmann sense, between vicinal groups, and not in the Meisenheimer sense between *anti* groups. The method also enables the structure of the oximes of the benzoins to be deduced. The structures of the corresponding desoxy compounds have been determined by a method also previously described[2] (Beckmann transformation of the first type). In the present paper, the benzoins and their oximes together with the derived desoxybenzoins and their oximes and transformation products are described.

A point of considerable importance in the study of mixed benzoins is whether both of the possible isomers are formed by the condensation of two different aldehydes in the presence of potassium cyanide, or whether only one is formed. In an earlier paper[3] the present authors reported that they had isolated two such isomers, using benzaldehyde and piperonal. The evidence was chiefly analytical. Tiffeneau and Lévy[4] have failed to isolate the two isomers. The present authors, after many attempts, have also failed to repeat the isolation of the two isomers. It now seems probable that the compound melting at 110° was a side-product such as benzyl piperonylate or piperonyl benzoate, of the same synoptic formula, isolated by chance. Unfortunately, none of the compound is now available to settle the point.

Tiffeneau and Lévy[4] believe that they have in two cases obtained evidence for the existence of pairs of isomeric benzoins. In work which was probably carried out simultaneously with Tiffeneau and Lévy's work, the present authors[5] have twice commented upon the ability of benzoins to form addition compounds, and it seems to them that Tiffeneau and Lévy's results could be readily explained on the basis of addition compound formation rather than on the basis of the formation of isomers. Thus in the condensation of piperonal and anisaldehyde, Tiffeneau and Lévy obtain two substances, melting at 75 and at 110°. The first is admittedly a mixture and gives on potash fission a mixture of piperonylic and anisic acids. In the hands of the present authors this substance, on oxidation with Fehling's solution, gave a mixture of about equal amounts of piperil and methoxymethylenedioxybenzil, showing the presence of considerable amounts of piperoin in the preparation. The substance melting at 110° similarly gave on oxidation, piperil, methoxymethylenedioxybenzil and anisil in the ratio 20:4:1 and is hence chiefly piperoin.

The other case is the condensation of benzaldehyde and *m*-methoxybenzaldehyde. The two products described by Tiffeneau and Lévy were

[2] Buck and Ide, THIS JOURNAL, **53**, 1536 (1931).

[3] Buck and Ide, *ibid.*, **52**, 220 (1930).

[4] Tiffeneau and Lévy, *Bull. soc. chim.*, [4] **49**, 725 (1931).

[5] Buck and Ide, THIS JOURNAL, **53**, 2350, 2784 (1931).

regenerated from a semicarbazone preparation. Both on potash fission gave benzoic and *m*-methoxybenzoic acids and so are not entities. No analyses are given, and the main product, m. p. 80°, is admittedly not pure.

It is evident that, by potash fission, the same acids would be obtained either from a mixture or addition compound of two simple benzoins, or from a mixture or addition compound of the corresponding pair of isomeric mixed benzoins.

In view of the above considerations, it would appear that the claim to have obtained evidence of two pairs of isomeric mixed benzoins requires further substantiation. It seems to the present authors that the evidence is strongly in favor of addition compounds. Benzoin reactions are, however, very susceptible to variations in experimental conditions, and unless these are exactly specified, it is not at all certain that two different workers will always reproduce each other's results.

The present authors therefore consider that no case of the formation of a pair of isomeric mixed benzoins has been conclusively demonstrated, and they are inclined to the belief that only one isomer is formed. Experimental proof, for or against, will be difficult on account of the possible complexity of the reaction mixtures (*cf.* Lachman[6]) and the probability that, if both isomers are formed, one will be present only in small amount.

It is intended to investigate the question of isomeric mixed benzoins from another angle, by regenerating the benzoins from the corresponding benzils, where isomerism and addition compound formation are not involved.

Note on Nomenclature.—The system earlier suggested by Buck and Ide[3] (depending on the termination -oin) is inadequate for the more highly substituted benzoins and derivatives. The authors therefore suggest using primes for the numbered substituents on the benzene ring next to the CO group (or in the case of oximes, the C=NOH group). This method has been followed in the present paper, using the full systematic name, however. In future, *o*-chlorobenzveratroin (old name) will be written 2-chloro-3′,4′-dimethoxybenzoin, and so on.

Experimental

Benzoins.—The benzoins not previously described were prepared by dissolving 0.2 mole of each aldehyde in 100 cc. of alcohol; 10 g. of potassium cyanide, dissolved in 20 cc. of water, was then added and the solution refluxed on the steam-bath for one to one and one-half hours. The crystalline products are obtained from the reaction mixtures by treatment with solvents and exposure to cold (refrigerator). Steam distillation to remove unchanged aldehydes was not resorted to, on account of the pos-

[6] Lachman, THIS JOURNAL, **46**, 708 (1924).

TABLE I

BENZOINS

	Benzoin	Aldehydes used	
I	2-Chloro-α-hydroxybenzyl-3′,4′-diethoxyphenyl ketone	2-Chlorobenz-	3,4-Diethoxybenz-[a]
J	2-Chloro-α-hydroxybenzyl-3′-ethoxy-4′-methoxyphenyl ketone	2-Chlorobenz-	3-Ethoxy-4-methoxybenz-[b]
K	2-Chloro-α-hydroxybenzyl-3′-methoxy-4′-ethoxyphenyl ketone	2-Chlorobenz-	3-Methoxy-4-ethoxybenz-[c]
L	3-Chloro-α-hydroxybenzyl-4′-dimethylaminophenyl ketone[7]	3-Chlorobenz-	4-Dimethylaminobenz-
M	4-Chloro-α-hydroxybenzyl-3′,4′-methylenedioxyphenyl ketone[7]	4-Chlorobenz-	Piperonal
N	3,4-Methylenedioxy-α-hydroxybenzyl-4′-dimethylaminophenyl ketone[8]	Piperonal	4-Dimethylaminobenz-

	Formula	M. p., °C.	Yield, %	Appearance	Analyses, % Calcd.		Found	
I	$ClC_6H_4CHOHCOC_6H_3(OC_2H_5)_2$	106	63	Stout prisms	C, 64.55	H, 5.72	C, 64.42	H, 5.65
J	$ClC_6H_4CHOHCOC_6H_3(OC_2H_5)OCH_3$	103	81	Fine needles	C, 63.63	H, 5.34	C, 63.71	H, 5.60
K	$ClC_6H_4CHOHCOC_6H_3(OCH_3)OC_2H_5$	120	60	Rhombs	C, 63.63	H, 5.34	C, 63.91	H, 5.49
L	$ClC_6H_4CHOHCOC_6H_4N(CH_3)_2$	140	45	Rhombs	Cl, 12.24		Cl, 11.98	
M	$ClC_6H_4CHOHCOC_6H_3O_2CH_2$	110	40	Needles	C, 61.95	H, 3.79	C, 61.81	H, 3.68
N	$CH_2O_2C_6H_3CHOHCOC_6H_4N(CH_3)_2$	136	40	Fern-like crystals	C, 68.19	H, 5.73	C, 68.47	H, 5.92
					N, 4.68		N, 4.77	

[a] Prepared by ethylating 3-ethoxy-4-hydroxybenzaldehyde with ethyl sulfate and sodium hydroxide. Described and prepared in another way by Gattermann, *Ann.*, **357,** 368 (1907).

[b] Prepared by methylating 3-ethoxy-4-hydroxybenzaldehyde with methyl sulfate and sodium hydroxide. Described and prepared in another way by Schorigin and co-workers, *Ber.*, **64,** 274 (1931).

[c] Prepared by ethylating vanillin with ethyl sulfate and sodium hydroxide. Described and prepared in another way by Tiemann, *Ber.*, **8,** 1127 (1875).

[7] Buck and Ide, THIS JOURNAL, **52,** 4107 (1930).

[8] Buck and Ide, *ibid.*, **53,** 2350 (1931).

sibilities of change in the reaction mixtures during the process. The benzoins, when crystallized from alcohol, are persistently yellow. Crystallization from acetic acid gives the benzoin in a pure white form. The results are given in Table I. Derived compounds, such as oximes, have the same letter as the parent benzoin.

Benzils.—The benzils were all prepared by dissolving the appropriate mixed benzoin in alcohol (usually 2.0 g. was taken) and oxidizing with a slight excess of Fehling's solution. The crude product was recrystallized from alcohol until pure.

TABLE II

BENZILS

	Benzil	M. p., °C.	Yield, %	Appearance	Analyses, % Calcd. C	Calcd. H	Found C	Found H
I	2-Chloro-3′,4′-diethoxy-	110	70	Yellow rhombs	64.94	5.15	64.92	5.07
J	2-Chloro-3′-ethoxy-4′-methoxy-	150	84	Yellow hexagons	64.03	4.74	64.20	5.01
K	2-Chloro-3′-methoxy-4′-ethoxy-	132	80	Yellow needles	64.03	4.74	64.36	5.08
L	3-Chloro-4′-dimethylamino-[7]	130	90	Amber plates	66.77	4.91	66.53	5.21
M	4-Chloro-3′,4′-methylenedioxy-[7]	132	78	Yellow needles	62.38	3.12	62.24	2.99
N	3,4-Methylenedioxy-4′-dimethylamino-	174	60	Yellow hexagons	68.65	5.08	68.84	5.21

Desoxy Compounds.—The desoxy compounds were prepared by the method previously described.[7] Alcohol is usually the best solvent for recrystallization. All the desoxy compounds are white. It will be seen that, with all the desoxy compounds below, the structure corresponds to that of the parent benzoin, the CHOH group being reduced to CH_2. This is not invariably the case.[1]

TABLE III

DESOXY COMPOUNDS

	Phenyl ketone	M. p., °C.	Yield, %	Appearance	Analyses, % Calcd. C	Calcd. H	Found C	Found H
I	2-Chlorobenzyl-3′,4′-diethoxy-	95	58	Long needles	67.79	6.01	67.63	6.21
J	2-Chlorobenzyl-3′-ethoxy-4′-methoxy-	98	57	Long needles	66.97	5.61	67.16	5.79
K	2-Chlorobenzyl-3′-methoxy-4′-ethoxy-	121	55	Long needles	66.97	5.62	67.28	5.83
L	3-Chlorobenzyl-4′-dimethylamino-[7]	125	80	Needles	70.18	5.89	69.90	5.99
M	4-Chlorobenzyl-3′,4′-methylenedioxy-[7]	113	80	Needles	65.56	4.01	65.72	4.09
N	3,4-Methylenedioxybenzyl-4′-dimethylamino-	140	44	Glittering plates	72.05	6.05	72.17	6.27

Oximes of Desoxy Compounds.—The oximes were prepared by one of the methods given in Part IV[1] for the benzoin oximes. The figure in the last column of the table refers to the preparation. All the oximes are white, well-crystallized compounds. They have, in every case, the *anti*-benzyl configuration.

The amides were identified either by hydrolysis and the identification of the acid so produced (the basic fragment is always decomposed) or by synthesis. The amides are very stable and require many hours' refluxing with concentrated hydrochloric acid in order to hydrolyze them. Amides I, J and K gave on hydrolysis *o*-chlorophenylacetic acid, identified by comparison and mixed melting point determinations with an authentic specimen. Amide L on hydrolysis gave *m*-chlorophenylacetic acid, identical

TABLE IV

OXIMES OF DESOXY COMPOUNDS

	Phenyl ketoxime	M. p., °C.	Yield, %	Appearance	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Method of prepn.
I	*Anti*-2-chlorobenzyl-3′,4′-diethoxy-	105	70	Slender needles	64.74	6.04	64.81	6.08	1
J	*Anti*-2-chlorobenzyl-3′-ethoxy-4′-methoxy-	130	63	Fine needles	63.82	5.67	63.98	5.89	1
K	*Anti*-2-chlorobenzyl-3′-methoxy-4′-ethoxy-	167	94	Needles	63.82	5.67	63.89	5.76	3
L	*Anti*-3-chlorobenzyl-4′-dimethylamino-	146	70	Slender prisms	66.52	5.93	66.79	6.03	1
M	*Anti*-4-chlorobenzyl-3′,4′-methylenedioxy-	119	55	Tiny hexagons	62.16	4.17	62.30	4.30	1
N	*Anti*-3,4-methylenedioxy-	152	70	Fine needles	68.42	6.08	68.67	6.20	3

TABLE V

AMIDES

	Anilide	M. p., °C.	Yield, %	Appearance	Analyses, % Calcd. C	Calcd. H	Found C	Found H
I	2-Chlorophenylacet-3′,4′-diethoxy-	178	50	Fine needles	64.74	6.04	65.13	6.21
J	2-Chlorophenylacet-3′-ethoxy-4′-methoxy-	165	60	Long needles	63.82	5.67	63.71	5.43
K	2-Chlorophenylacet-3′-methoxy-4′-ethoxy-	166	60	Slender prisms	63.82	5.67	63.97	6.00
L	3-Chlorophenylacet-4′-dimethylamino-	178	50	Tiny needles	66.52	5.93	66.82	6.10
M	4-Chlorophenylacet-3′,4′-methylenedioxy-	195	80	Tiny needles	62.16	4.17	62.40	4.49
N	3,4-Methylenedioxyphenylacet-4′-dimethylamino-	170	40	Tiny needles	68.42	6.08	68.58	6.13

with a specimen prepared as described below. Amide M on hydrolysis gave *p*-chlorophenylacetic acid, identical with a specimen prepared by the method of Petrenko-Kritschenko, *Ber.*, **25**, 2239 (1892). Amide N was identified with a synthetic specimen prepared from homopiperonoyl chloride and dimethyl-*p*-phenylenediamine hydrochloride, by the Schotten–Baumann method.

***m*-Chlorophenylacetic Acid. Azlactone.**[9]—One-tenth mole of *m*-chlorobenzaldehyde, 0.1 mole of hippuric acid and 0.1 mole of freshly-fused, powdered, anhydrous sodium acetate are mixed with 0.3 mole of acetic anhydride and the mixture heated on a hot-plate, with constant stirring, until liquid. The flask is then at once transferred to a water-bath and heated for 105 minutes. After cooling, the magma is stirred with an equal volume of alcohol and left overnight. The crystals are then filtered off and washed with a little cold alcohol and then with hot water. The azlactone forms a mass of canary-yellow crystals. The yield is 63%. After recrystallization from alcohol the compound melts at 164°.

Anal. Calcd. for $C_{16}H_{10}O_2NCl$: C, 67.71; H, 3.55. Found: C, 67.93; H, 3.93.

***m*-Chlorophenylpyruvic Acid.**—Fifteen grams of azlactone is refluxed (oil-bath) with 100 cc. of 10% sodium hydroxide solution for four hours. The mixture, after cooling, is saturated with sulfur dioxide (temperature below 40°), and the benzoic acid filtered off and washed with a little water. The filtrate and washings are then heated nearly to boiling and concentrated hydrochloric acid added cautiously, in small

[9] *Cf.* Kropp and Decker, *Ber.*, **42**, 1188 (1909).

portions, until excess is present. The mixture is gently boiled for a short time, then cooled and the *m*-chlorophenylpyruvic acid filtered off and washed with water. The yield is 8.1 g. (77%). Recrystallized from acetic acid, the compound forms white, tiny, felted needles, melting at 145°.

Anal. Calcd. for $C_9H_7O_3Cl$: C, 54.43; H, 3.55. Found: C, 54.60; H, 3.79.

***m*-Chlorophenylacetic Acid.**[10]—Six grams of the pyruvic acid, dissolved in a solution of 8.0 g. of sodium hydroxide in 25 cc. of water, together with 10 g. of ice, is treated with a solution of 7.5 g. of superoxol (30% H_2O_2) in 15 cc. of water. The addition is carried out slowly, with cooling and shaking. After standing for five hours the solution

TABLE VI

BENZOIN OXIMES

The oximes were prepared by the methods given in Part IV.[1] The numbers refer to these preparations. All the oximes are of the α (*anti* phenyl) form.

	Ketoxime	M. p., °C.	Yield, %	Appearance	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Method of prepn.
I	2-Chloro-α-hydroxybenzyl-3′,4′-diethoxyphenyl-	*ca.* 61	59	Obscure	61.78	5.76	61.90	5.72	1
J	2-Chloro-α-hydroxybenzyl-3′-ethoxy-4′-methoxyphenyl-	113	80	Irreg. plates	60.78	5.40	60.68	5.38	2
K	2-Chloro-α-hydroxybenzyl-3′-methoxy-4′-ethoxyphenyl-	114	71	Hexagons	60.78	5.40	60.97	5.66	2
L	3-Chloro-α-hydroxybenzyl-4′-dimethylamino-	148	57	Tiny needles	63.03	5.62	63.30	5.75	2
M	4-Chloro-α-hydroxybenzyl-3′,4′-methylenedioxyphenyl-	178	40	Fine needles	58.91	3.95	59.21	4.08	2
N	3,4-Methylenedioxy-α-hydroxybenzyl-4′-dimethylamino-	145	71	Fine prisms	64.93	5.77	65.10	5.81	2

TABLE VII

BECKMANN REACTION

The reaction was carried out as previously described, using benzene sulfone chloride and alkali.[1] The residues from oximes I and N were very small. In all the other cases a considerable residue remained after fractionation. The reaction mixtures were fairly clean, except in the cases of oximes L and M, where considerable tarry matter was formed. In no case was there more than a trace of isonitrile odor.

		1st Fraction			2d Fraction		
Oxime	Taken, g.	Name, aldehyde	Yield g.	Yield %	Name, nitrile	Yield g.	Yield %
I	17	*o*-Chlorobenz-[a]	6.0	88	3,4-Diethoxybenzo-[c]	8.0	87
J	12	*o*-Chlorobenz-[a]	3.7	73	3-Ethoxy-4-methoxybenzo-[c]	2.8	44
K	12	*o*-Chlorobenz-[a]	3.3	65	3-Methoxy-4-ethoxybenzo-[d]	3.8	60
L	6.7	*m*-Chlorobenz-[a]	1.6	52	*p*-Dimethylaminobenzo-[e]	2.0	62
M	6.0	*p*-Chlorobenz-[a]	1.4	38	Pipero-[e]	1.8	47
N	8.0	Piperonal[b]	3.1	77	*p*-Dimethylaminobenzo-[e]	2.5	63

[a] Converted into the acid and identified by mixed melting point determinations with an authentic specimen. [b] Identified by mixed melting point determinations with the authentic aldehyde. [c] Identified by mixed melting point determinations with a specimen of nitrile prepared as described below. [d] Identified by mixed melting point determinations with a specimen of authentic nitrile prepared by the action of acetic anhydride on the corresponding oxime. Previously obtained by Keffler, *J. Chem. Soc.*, **119**, 1476 (1921). [e] Identified by comparison with the authentic nitrile prepared as in Part IV.[1]

[10] *Cf.* Mauthner, *Ann.*, **370**, 375 (1909).

is cautiously acidified with hydrochloric acid, and, while still warm, extracted with benzene. The extract is dried and the benzene evaporated. After recrystallization from aqueous alcohol, the acid forms large, pearly leaflets, melting at 74°. The yield is 3.0 g. (57%).

Anal. Calcd. for $C_8H_7O_2Cl$: C, 56.29; H, 4.13. Found: C, 56.00; H, 4.26.

3,4-Diethoxybenzaldoxime was prepared by the action of hydroxylamine acetate on the aldehyde. The oxime forms tiny needles melting at 98°.

Anal. Calcd. for $C_{11}H_{15}O_3N$: C, 63.12; H, 7.23. Found: C, 63.55; H, 7.33.

3,4-Diethoxybenzonitrile was prepared by refluxing the above oxime with acetic anhydride for two hours, and pouring the mixture into water. When recrystallized from aqueous alcohol, the nitrile forms long, flat prisms, melting at 68°.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.07; H, 6.85. Found: C, 69.25; H, 7.00.

3-Ethoxy-4-methoxybenzaldoxime, prepared by means of hydroxylamine acetate, forms fine needles, melting at 98°.

Anal. Calcd. for $C_{10}H_{13}O_3N$: C, 61.50; H, 6.71. Found: C, 61.85; H, 6.86.

3-Ethoxy-4-methoxybenzonitrile was prepared from the above oxime by refluxing with acetic anhydride for two hours and pouring the reaction mixture into water. Recrystallized from aqueous alcohol it forms a mass of tiny needles melting at 70°.

Anal. Calcd. for $C_{10}H_{11}O_2N$: C, 67.76; H, 6.26. Found: C, 68.00; H, 6.30.

3-Methoxy-4-ethoxybenzaldoxime, prepared in the usual way by means of hydroxylamine acetate, forms tiny needles, melting at 100°.

Anal. Calcd. for $C_{10}H_{13}O_3N$: C, 61.50; H, 6.71. Found: C, 61.63; H, 6.65.

Summary

The structures of six mixed benzoins and their oximes, together with the corresponding desoxy compounds and their oximes, have been determined. The benzils and Beckmann transformation products are also described.

The question of the formation of pairs of isomeric mixed benzoins (by the potassium cyanide condensation) is discussed. It is considered that reported cases of the occurrence of such pairs of isomers require further substantiation.

TUCKAHOE, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NEBRASKA]

THE CONDENSATION OF 3-NITRO-4-HALOGENO-PHENYLARSONIC ACIDS WITH ALIPHATIC AMINO COMPOUNDS AND PHENOLS

BY W. D. MACLAY[1] AND CLIFF S. HAMILTON

RECEIVED MARCH 26, 1932 PUBLISHED AUGUST 5, 1932

Aromatic arsonic acid derivatives containing both primary and secondary amino groups have not been studied as extensively as those containing only a primary amino group; and arsonic acid derivatives containing more than one aromatic nucleus, the second substituted nucleus being attached to that containing the arsono group by the linkage of oxygen, have been studied hardly at all. A common method for synthesizing types of compounds such as these is through the substitution of nuclear halogen. It has long been known that this replacement could be brought about by the ordinary reagents employed in the aliphatic series, only when the attachment of the halogen was loosened by the presence of certain groups, such as nitro, cyano, carboxyl, arsono, etc. Gibson and others[2] successfully applied the method of Ullmann[3] to condensation reactions of *o*-bromophenylarsonic acid with aromatic amines. In an analogous manner Etzelmiller and Hamilton[4] condensed *o*-chlorophenylarsonic acid with aliphatic amines, aliphatic alcohols and phenol.

Boehringer and Soehne[5] showed that 3-nitro-4-chlorophenylarsonic acid and glycine reacted in an alkaline solution to give 2-nitro-4-arsonophenylglycine. King[6] condensed the same arsonic acid with piperidine in an alcoholic solution to form 3-nitro-4-piperidinophenylarsonic acid. Fourneau and Funke[7] showed that 3-nitro-4-chlorophenylarsonic acid reacted with ethylenediamine and piperazine in the presence of anhydrous sodium acetate. This reaction has been further extended by Barber,[8] who prepared a series of diphenylamine derivatives through the condensation of 3-nitro-4-chlorophenylarsonic acid with various substituted aromatic amines in aqueous alkaline solution. Thus, the reactivity of the halogen in 3-nitro-4-halogenophenylarsonic acids suggested the use of these compounds in condensation reactions with aliphatic amino compounds and substituted phenols leading to two series of arsenicals.

[1] Parke, Davis and Company Fellow.

[2] Burton and Gibson, *J. Chem. Soc.*, 247 (1927); Gibson and Johnson, *ibid.*, 2499 (1927); 2204 (1928).

[3] Ullmann, *Ann.*, **355**, 312 (1907).

[4] Etzelmiller and Hamilton, THIS JOURNAL, **53**, 3085 (1931).

[5] Boehringer and Soehne, German Patent 285,604.

[6] King, *J. Chem. Soc.*, 1053 (1927).

[7] Fourneau and Funke, *Bull. soc. chim.*, **43**, 889 (1928).

[8] Barber, *J. Chem. Soc.*, 471 (1929).

A series of condensation reactions was carried out with 3-nitro-4-halogenophenylarsonic acids and various aliphatic primary amines. The amines, iso- and *n*-amyl, iso- and *n*-butyl, *n*-propyl and ethanol, condensed with the arsonic acid in aqueous alkaline solution. The reaction worked equally well in an anhydrous mixture of potassium carbonate and *n*-amyl alcohol, but the ease of carrying out the condensation and purification of the reaction product favored the former method. Three hours at temperatures of 125–135° was found to be sufficient time for obtaining maximum yields in this type of condensation.

Glycine readily condensed with 3-nitro-4-halogenophenylarsonic acids in an anhydrous mixture of potassium carbonate, *n*-amyl alcohol and copper powder, to give good yields of 2-nitro-4-arsonophenylglycine.

The amino derivatives of the condensation products of the aliphatic primary amines with 3-nitro-4-halogenophenylarsonic acids were prepared in yields of 40–48% by the method of Jacobs, Heidelberger and Rolf.[9]

The free base, 2-amino-4-arsonophenylglycine, was not isolated when the corresponding nitro derivative was reduced. In every instance, 2-oxy-3-dihydroquinoxaline-7-arsonic acid,[10] was obtained through the elimination of water.

A series of condensation reactions was also carried out with substituted phenols. These reactions took place only in an anhydrous medium. Phenol-, *p*-chlorophenol, *o*- and *p*-cresols and *p*-nitrophenol reacted with 3-nitro-4-bromophenylarsonic acid to form the corresponding phenyl ether derivatives. Under similar conditions, salicylic acid, *o*-nitrophenol, salicylic aldehyde and *p*-hydroxybenzaldehyde failed to condense.

The amino derivatives of these phenyl ethers were prepared by means of reduction with alkaline ferrous hydroxide. When 2-amino-4-arsono-2′-carboxyphenyl ether was heated above 200°, water was eliminated, leading to the formation of the corresponding lactam.

It was considered desirable to study the reaction of 3-nitro-4-bromophenylarsonic acid with aliphatic alcohols. The alcohols, iso- and *n*-amyl, and *n*-butyl, were included in this study. The general procedure was to heat a mixture of 10 g. of 3-nitro-4-bromophenylarsonic acid, 10 g. of anhydrous potassium carbonate, 0.2 g. of copper powder and 35 cc. of the alcohol containing either potassium or sodium, in amounts varying from 1 to 2.5 g., for ten hours at refluxing temperature, with stirring. In no case was a condensation product isolated. Condensation reactions with isoamyl alcohol invariably led to tarry formations from which nothing was isolated. With *n*-butyl alcohol, although the alcohol had been carefully dried and distilled, as high as 50% of the compound was hydrolyzed to 3-nitro-4-hydroxyphenylarsonic acid. The water present was

[9] Jacobs, Heidelberger and Rolf, THIS JOURNAL, **40**, 1581 (1918).

[10] Ewins, Newbery and Stickings, *J. Chem. Soc.*, 851 (1927).

possibly due to the formation of the double potassium salt of the arsonic acid group.

In beginning a study of the activity of the halogen in the para-position with respect to the arsonic acid group, a series of condensation reactions with aniline was carried out under varying experimental conditions. The halogenophenylarsonic acid employed in these reactions was *p*-bromophenylarsonic acid. The general procedure was to heat 10 g. of *p*-bromophenylarsonic acid, 10 g. of anhydrous potassium carbonate, 0.2 g. of catalyst and varying amounts of aniline and amyl alcohol, which was used as a solvent at different temperatures, in an Erlenmeyer flask fitted with a condenser with a ground-glass connection and mechanical stirrer. Only two catalysts, copper powder and cuprous iodide, were tried in this series of reactions while *n*-amyl alcohol was the only solvent employed. The temperatures varied from 90 to 220°, the time from ten to eighty hours and the amounts of aniline and amyl alcohol from 0 cc. to 30 cc. In some instances sealed tube reactions were employed. In no case was a substance isolated which would give the slightest qualitative test for nitrogen. In all cases from 40–80% of the original arsonic acid was recovered.

Incidentally, the halogen in *p*-bromophenylarsonic acid was not hydrolyzed when refluxed for forty-eight hours in 3 *N* sodium hydroxide solution.

Experimental[11]

General Procedure for the Preparation of 3-Nitro-4-alkylaminophenylarsonic Acids.—Twelve grams of 3-nitro-4-chlorophenylarsonic acid, 40 cc. of 2 *N* sodium hydroxide, 6 cc. of the primary alkylamine and 25 cc. of water in a 200-cc. Erlenmeyer flask, fitted with a condenser, were heated in an oil-bath at 125–135° for three hours. On acidification to Congo red paper with 6 *N* hydrochloric acid, an orange colored oil separated which on cooling solidified to a yellow crystalline mass. This was redissolved in sodium carbonate solution, acidified to litmus paper and boiled with decolorizing carbon. The arsonic acid was again precipitated with hydrochloric acid and further purified by recrystallizing from dilute acetic acid. These compounds did not melt or decompose below 250°.

TABLE I

3-NITRO-4-ALKYLAMINOPHENYLARSONIC ACIDS

-Aminophenyl-arsonic acid	Yield, %	Formula	Arsenic analyses, % Calcd.	Found	
3-Nitro-4-propyl-	68	$C_9H_{13}O_5N_2As$	24.67	24.60	24.58
3-Nitro-4-butyl-	62	$C_{10}H_{15}O_5N_2As$	23.58	23.62	23.63
3-Nitro-4-isobutyl-	60	$C_{10}H_{15}O_5N_2As$	23.58	23.57	23.48
3-Nitro-4-amyl-	85	$C_{11}H_{17}O_5N_2As$	22.59	22.70	22.70
3-Nitro-4-isoamyl-	80	$C_{11}H_1\ O_5N_2As$	22.59	22.65	22.74
3-Nitro-4-β-hydroxyethyl	74	$C_8H_{11}O_6N_2As$	24.51	24.46	24.50

2-Nitro-4-arsonophenylglycine.[12]—A mixture of 15 g. of 3-nitro-4-bromophenylarsonic acid, 12 g. of anhydrous potassium carbonate, a trace of copper powder, 6 g. of

[11] Cislak and Hamilton, THIS JOURNAL, **52**, 638 (1930).

[12] Boehringer and Soehne, German Patent 285,604.

glycine and 35 cc. of *n*-amyl alcohol in a 200-cc. Erlenmeyer flask fitted with a ground-glass connection was heated for seven hours in an oil-bath at 150°. The reaction mixture was agitated by means of a mechanical stirrer extending down through the condenser. The reaction mixture was cooled and the amyl alcohol removed by decantation. The mass remaining was dissolved in 75 cc. of hot water and acidified to Congo red paper with hydrochloric acid. A dark brown crystalline mass separated. This was further purified by reprecipitating from sodium carbonate solution and recrystallization from acetic acid. The arsonic acid separated from this solvent in the form of light yellow needles decomposing at 230–235°. The yield was 9.0 g. or 61% of the calculated amount.

Anal. Calcd. for $C_8H_9O_4N_2As$: As, 23.44. Found: As, 23.50, 23.55.

General Procedure for the Preparation of 3-Amino-4-alkylaminophenylarsonic Acids.—The method employed for the preparation of these compounds was that described by Jacobs, Heidelberger and Rolf,[9] an alkaline ferrous hydroxide reduction. Recrystallized from 75% methyl alcohol, the free bases separated in the form of white needles which assumed a grayish or pink color after exposure to the air for a few moments.

TABLE II

3-AMINO-4-ALKYLAMINOPHENYLARSONIC ACIDS

Aminophenyl-arsonic acid	Yield, %	Formula	Arsenic analyses, % Calcd.	Found	
3-Amino-4-propyl-	66	$C_9H_{15}O_3N_2As$	27.37	27.31	27.39
3-Amino-4-butyl-	66	$C_{10}H_{17}O_3N_2As$	26.04	25.98	25.99
3-Amino-4-isobutyl-	66	$C_{10}H_{17}O_3N_2As$	26.04	25.90	25.92
3-Amino-4-amyl-	73	$C_{11}H_{19}O_3N_2As$	24.83	24.87	24.96
3-Amino-4-isoamyl-	67	$C_{11}H_{19}O_3N_2As$	24.83	24.93	24.77
3-Amino-4-β-hydroxy-ethyl-[a]	39	$C_8H_{13}O_4N_2As$	27.17	27.15	27.15

[a] I. D. Farbenind A.-G., German Patent 530,397 (1928).

2-Oxy-3-dihydroquinoxaline-7-arsonic Acid.[10]—When 2-nitro-4-arsonophenylglycine was reduced with alkaline ferrous hydroxide, a quinoxaline derivative was formed through the loss of water. The free base was not isolated, the ring compound separating from the filtrate when it was acidified to Congo red paper. Recrystallized from 75% methyl alcohol, 2-oxy-3-dihydroquinoxaline-7-arsonic acid separated in long white needles, yield 70%.

Anal. Calcd. for $C_8H_9O_4N_2As$: As, 27.57; N, 10.28. Found: As, 27.65, 27.59; N, 10.15.

The Condensation of 3-Nitro-4-bromophenylarsonic Acid with Phenols.—A mixture of 10 g. of 3-nitro-4-bromophenylarsonic acid, 10 g. of anhydrous potassium carbonate, a trace of copper powder, a small excess of an equivalent amount of the phenol and 35 cc. of *n*-amyl alcohol in a 200-cc. Erlenmeyer flask fitted with a ground-glass connection was heated for six to eight hours in an oil-bath at 140–150°, the reaction mixture being well stirred. The excess phenol and amyl alcohol were removed by steam distillation, and the resulting solution was treated with decolorizing carbon. On acidification to Congo red paper with dilute hydrochloric acid a brownish mass separated which was further purified through crystallization from acetic acid. These phenyl ether derivatives separated from this solvent in the form of a white crystalline mass. Phenol, *p*-chlorophenol, *p*-cresol, *o*-cresol and *p*-nitrophenol were condensed with the 3-nitro-4-bromophenylarsonic acid in this manner. The carboxyl derivatives were prepared through oxidation of the corresponding methyl derivatives with alkaline permanganate. They do not melt or decompose below 250°.

TABLE III

2-NITRO-4-ARSONOPHENYL ETHER DERIVATIVES

2-Nitro-4-arsono-	Yield, %	Formula	Arsenic analyses, % Calcd.	Found	
-Phenyl ether	54	$C_{12}H_{10}O_6NAs$	22.11	22.05	21.97
-4'-Chlorophenyl ether	78	$C_{12}H_9O_6NClAs$	20.08	20.21	19.92
-4'-Methylphenyl ether	46	$C_{13}H_{12}O_6NAs$	21.25	21.35	21.27
-4'-Carboxyphenyl ether	60	$C_{13}H_{10}O_8NAs$	19.58	19.61	19.66
-2'-Methylphenyl ether	25	$C_{13}H_{12}O_6NAs$	21.25	21.35	21.27
-2'-Carboxyphenyl ether	82	$C_{13}H_{10}O_8NAs$	19.58	19.70	19.67
-4'-Nitrophenyl ether	10	$C_{12}H_9O_8N_2As$	19.53	19.74	19.67

2-Amino-4-arsonophenyl Ether Derivatives.—These compounds were prepared by reducing the corresponding nitro derivatives with alkaline ferrous hydroxide in a manner previously described.

TABLE IV

2-AMINO-4-ARSONOPHENYL ETHER DERIVATIVES

2-Amino-4-arsono-	Yield, %	Formula	Arsenic analyses, % Calcd.	Found	
-Phenyl ether	57	$C_{12}H_{12}O_4NAs$	24.27	24.29	24.34
-4'-Chlorophenyl ether	66	$C_{12}H_{11}O_4NClAs$	21.84	21.81	21.92
-4'-Carboxyphenyl ether	73	$C_{13}H_{12}O_6NAs$	21.25	21.28	21.23
-2'-Methylphenyl ether	45	$C_{13}H_{14}O_4NAs$	23.22	23.22	23.20
-2'-Carboxyphenyl ether	58	$C_{13}H_{12}O_6NAs$	21.25	21.27	21.21

2-Amino-4-arsono-2'-carboxyphenyl Ether Lactam.—Three grams of 2-amino-4-arsono-2'-carboxyphenyl ether was placed in a hard-glass test-tube fitted with a suction apparatus. The tube was placed in an oil-bath at 200–210°. At this temperature water was eliminated. Heating was continued for twenty minutes, after which the reaction mixture was dissolved in dilute sodium hydroxide and treated with decolorizing carbon. After precipitation with hydrochloric acid, the lactam was further purified by recrystallizing from 150 cc. of 75% acetic acid. It separated from this solvent in white rectangular plates; yield 2 g. or 70%. It does not melt or decompose below 250°.

Anal. Calcd. for $C_{13}H_{10}O_5NAs$: As, 22.39: N, 4.18. Found: As, 22.41, 22.44; N, 4.06, 3.97.

4-Arsono-4'-methylphenyl Ether.—Twenty grams of 4-amino-4'-methylphenyl ether was dissolved in 24 cc. of hydrochloric acid (sp. gr. 1.18) and 400 cc. of water. This solution was diazotized at 0° with a solution of 7 g. of sodium nitrite in 50 cc. of water in the usual manner. After neutralizing the diazo solution to Congo red paper with 2 *N* sodium carbonate solution, it was added to a solution of sodium arsenate at 0°, which had been prepared by dissolving 30 g. of arsenious oxide in 300 cc. of 2 *N* sodium carbonate to which had been added a solution of 1 g. of copper sulfate dissolved in 25 cc. of water. After stirring for two hours, the reaction mixture was concentrated to 400 cc. on a steam-bath, treated with decolorizing carbon and the arsonic acid precipitated with hydrochloric acid. It was further purified through recrystallization from 75% acetic acid as white plates; yield, 47%. It did not melt or decompose below 250°.

Anal. Calcd. for $C_{13}H_{13}O_4As$: As, 24.35. Found: As, 24.32, 24.28.

4-Arsono-4'-carboxyphenyl Ether.—This compound was prepared by oxidizing the corresponding methyl derivative in alkaline permanganate solution; yield, 84%. It did not melt or decompose below 250°.

Anal. Calcd. for $C_{13}H_{11}O_6As$: As, 22.19. Found: As, 22.13, 22.11.

Summary

1. Condensation reactions with 3-nitro-4-halogenophenylarsonic acids and a series of aliphatic amino compounds, namely, iso- and *n*-amyl, iso- and *n*-butyl, *n*-propyl and ethanol amines, and glycine were successfully completed.

2. The corresponding amino derivatives of the above condensation products were prepared.

3. 3-Nitro-4-bromophenylarsonic acid was condensed with phenol and a series of substituted phenols, namely, *p*-chlorophenol, *o*- and *p*-cresols and *p*-nitrophenol, leading to a series of phenyl ether derivatives. The carboxyl derivatives were also prepared through the oxidation of the methyl derivatives.

4. The corresponding amino derivatives of the substituted phenol condensation products were synthesized. The lactam of 2-amino-4-arsono-2′-carboxyphenyl ether was obtained through the elimination of water from 2-amino-4-arsono-2′-carboxyphenyl ether. This resulted in the formation of a seven-membered ring compound.

5. A study was made of the effects of experimental conditions on the reaction of *p*-bromophenylarsonic acid with aniline.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN & FINK, INC.]

HALOGEN DERIVATIVES OF MONOHYDROXYDIPHENYLMETHANE AND THEIR ANTIBACTERIAL ACTION

BY EMIL KLARMANN, LOUIS W. GATES AND VLADIMIR A. SHTERNOV

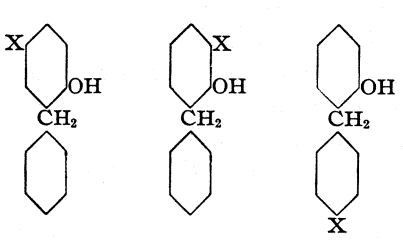
RECEIVED MARCH 29, 1932 PUBLISHED AUGUST 5, 1932

It was shown in a recent communication that monosubstituted halogen derivatives of 2,4-dihydroxydiphenylmethane are potent bactericides for *Eberthella typhi* and *Staphylococcus pyogenes aureus*.[1] Distinct differences in antibacterial action were observed depending upon the position of the substituting halogen. Thus with both the chloro and the bromo derivatives, it was found that a greater germicidal efficacy toward both test microörganisms was obtained in the case of substitution in the nucleus bearing the two hydroxyl groups than in that of substitution in the other nucleus. While *E. typhi* appeared to be more susceptible to the action of the compounds of this group than *Staph. aureus* the differences in susceptibility were by no means indicative of bactericidal specificity.

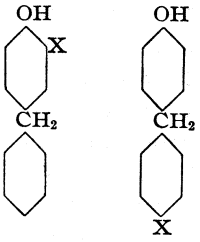
Notes on the Preparation of Halogen Hydroxydiphenylmethane Derivatives.—In continuing our studies on related problems, we devoted

[1] Klarmann and Von Wowern, THIS JOURNAL, **51**, 605 (1929).

our attention to the substitution by halogen of the 2- and 4- monohydroxydiphenylmethanes and of some of their alkyl derivatives, and to the antibacterial action of the compounds thus obtained. The two groups of compounds studied may be represented schematically by the following structural formulas (where X stands for the halogen)



Group I
Derived from 2-hydroxydiphenylmethane



Group II
Derived from 4-hydroxydiphenylmethane

In addition, a number of dihalogen substituted derivatives were prepared which may be regarded as combinations of the types within each group. The alkyl homologs studied contain the substituting alkyl radicals in the nucleus bearing the hydroxyl group.

The different compounds were obtained by condensation of a benzyl or halogen benzyl derivative with a phenol derivative substituted by halogen only or by halogen and alkyl groups. In the preparation of these substances advantage was taken of the following facts: condensation in the presence of "acid" agents, such as anhydrous zinc chloride, sulfuric acid, etc., leads predominantly to substitution in para-position to the phenolic hydroxyl group if the para-position is open, and to substitution in ortho-position if it is not; on the other hand, condensation according to Claisen leads primarily to substitution in ortho-position to the hydroxyl group.[2]

The 3-methyl-5-chloro-2-hydroxydiphenylmethane was obtained by benzylation of *o*-cresol according to Claisen and subsequent chlorination.

Benzylation of 4-chloro-*m*-cresol (6-chloro-3-hydroxy-1-methylbenzene) according to Claisen might yield two ortho-substituted derivatives, *viz.*, 5-chloro-4-methyl-2-hydroxydiphenylmethane or 5-chloro-6-methyl-2-hydroxydiphenylmethane; possibly a mixture of both is formed. We have made no attempt as yet to establish the position of the methyl group in this product which will be referred to hereafter as 5-chloro-4[6]-methyl-2-hydroxydiphenylmethane.

It is evident that some of the compounds under discussion should permit preparation by either method of condensation. This was actually found to be the case in a number of instances whereby additional evidence was obtained in support of the constitution attributed to the compounds studied.

[2] L. Claisen, *Ann.*, **442**, 210 (1925).

Action on Bacteria

(a) **Bactericidal Effects.**—The researches on the relation between the chemical constitution and the bactericidal action of organic compounds heretofore published point to the great usefulness of testing the effect of the chemicals upon as many microörganisms as possible. In the present investigation four bacterial species were used, *viz.*, two representatives of the Gram-positive and two of the Gram-negative microörganisms. Thus *Staphylococcus pyog. aureus* and *Streptococcus* (hemolytic strain) are representatives of the former, *Eberthella typhi* and *Eberthella paradysenteriae* (Flexner) of the latter class. This procedure appears desirable in view of the findings obtained with other related groups of organic compounds which seem to point distinctly to a class specificity for Gram-positive bacteria in a number of instances.[3] The data reported in the present paper indicate that most of the compounds studied show a similarly specific action; while practically all the compounds under consideration may be regarded quite generally as potent germicides, several of them are many times more effective against Staphylococcus and Streptococcus than against the bacilli of typhoid and paradysentery. It is of interest that similar effects have been observed by several investigators in the case of the inhibitory action of certain basic dyes of high molecular weight, particularly in the triphenylmethane series.

Table I gives a list of the compounds studied, the minimum average concentrations which are capable of killing the four microörganisms at 37° in five, ten and fifteen minutes, respectively, and the "phenol coefficients" calculated from a comparison of this effect with that produced by phenol under the same experimental conditions.

Table I indicates that this series of compounds comprises some very powerful bactericides. The action upon the Gram-positive microbes appears to be generally considerably stronger than upon the Gram-negative. Within the two classes of germs, *E. typhi* is somewhat more resistant than *E. paradysenteriae*, and staphylococcus more so than streptococcus.

When considering the two groups of monohalogen compounds studied, *viz.*, those derived from 2-hydroxydiphenylmethane and those derived from 4-hydroxydiphenylmethane, one cannot say that generally one or the other group is distinguished by greater antibacterial potency. However, certain regularities of behavior toward the microbes are distinctly evident, such as: that the 5-halogen-2-hydroxydiphenylmethanes are more potent than the 3-halogen-4-hydroxydiphenylmethanes, or that the monobromo derivatives of both the 2- and the 4-hydroxydiphenylmethanes are less effective than the corresponding monochloro derivatives against the two Gram-negative microörganisms, but more so against the Gram-positive. The 4′-chloro-2-hydroxydiphenylmethane is less effective than the 4′-chloro-4-hydroxydi-

[3] Klarmann, Gates and Shternov, THIS JOURNAL, **54**, 1204 (1932).

TABLE I

BACTERICIDAL ACTION

Derivatives of hydroxydiphenylmethane	*Staph. aureus*				*Strept. (hemol.)*				*E. typhi*				*E. paradysenteriae*			
	5 min.	10 min.	15 min.	Phenol coeff.	5 min.	10 min.	15 min.	Phenol coeff.	5 min.	10 min.	15 min.	Phenol coeff.	5 min.	10 min.	15 min.	Phenol coeff.
3-Chloro-4-	1: 9,000	1:10,000	1:10,000	125	1:12,000	1:13,000	1:14,000	165	1: 5,000	1: 5,000	1: 5,500	36	1: 7,000	1: 7,000	1: 7,000	54
3-Bromo-4-	1:13,000	1:14,000	1:15,000	170	1:13,000	1:15,000	1:16,000	185	1: 2,500	1: 2,500	1: 3,250	19	1: 5,000	1: 5,000	1: 5,000	37
3-Chloro-2-	1: 5,500	1: 5,500	1: 6,000	71	1: 7,000	1: 8,500	1: 9,000	94	1: 3,250	1: 3,750	1: 3,750	24	1: 3,750	1: 5,000	1: 5,000	36
4'-Chloro-4-	1:11,000	1:12,000	1:14,000	170	1:12,000	1:15,000	1:16,000	165	1:12,000	1:12,000	1:14,000	83	1:13,000	1:13,000	1:14,000	98
5-Chloro-2-	1:15,000	1:16,000	1:18,000	215	1:18,000	1:18,000	1:22,500	245	1: 9,000	1:10,000	1:13,000	74	1:11,000	1:12,000	1:13,000	92
5-Bromo-2-	1:20,000	1:22,500	1:25,000	295	1:25,000	1:27,500	1:27,500	310	1: 3,500	1: 3,500	1: 4,000	26	1: 6,500	1: 7,000	1: 8,000	55
4'-Chloro-2-	1:14,000	1:15,000	1:15,000	190	1:14,000	1:14,000	1:18,000	175	1: 7,000	1: 8,000	1: 8,000	57	1:11,000	1:12,000	1:15,000	90
3,4'-Dichloro-4-	1:20,000	1:25,000	1:30,000	345	1:15,000	1:18,000	1:22,500	175	1: 5,500	1: 6,500	1: 7,000	41	1:14,000	1:15,000	1:15,000	110
3-Chloro-4'-bromo-4-	Indefinite over 10,000			200	1:40,000	1:40,000	1:50,000	565	1: 2,500	1: 2,500	1: 2,500	17	1: 3,000	1: 3,000	1: 3,250	24
3,5-Dichloro-2-	1: 5,000	1: 6,000	1: 6,000	65	1:20,000	1:22,500	1:22,500	250	1: 3,000	1: 3,000	1: 3,250	22	1:11,000	1:12,000	1:12,000	85
5-Chloro-3-methyl-2-	1:18,000	1:18,000	1:20,000	245	1:27,500	1:30,000	1:30,000	300	1: 2,000	1: 2,500	1: 2,500	16	1: 3,250	1: 3,500	1: 3,750	25
4'-Chloro-3-methyl-2-	1:16,000	1:20,000	1:20,000	240	1:20,000	1:25,000	1:27,500	260	1: 2,000	1: 2,250	1: 2,500	16.0	1: 3,500	1: 3,750	1: 3,750	26
5-Chloro-4[6]-methyl-2-	1:30,000	1:30,000	1:32,500	405	1:35,000	1:35,000	1:45,000	455	1: 2,250	1: 2,750	1: 2,750	17	1: 3,500	1: 4,500	1: 5,000	34
5-Chloro-4,6-dimethyl-2-	1:70,000	1:80,000	1:80,000	920	1:55,000	1:70,000	1:80,000	785	1: 3,750	1: 4,500	1: 5,000	31	1: 2,750	1: 3,000	1: 3,250	22
4'-Bromo-4,6-dimethyl-2-	1:30,000	1:35,000	1:35,000	420	1:50,000	1:60,000	1:70,000	600	.....	.....	.....	..	.....	.....	.....	..
5-Chloro-3-iso-propyl-6-methyl-2-	1: 2,250	1: 3,000	1: 3,250	35	1: 2,750	1: 3,000	1: 3,250	38	1: 2,000	1: 2,250	1: 2,500	16	1: 2,000	1: 2,000	1: 2,500	15
Phenol (control)	1: 70	1: 80	1: 80	1	1: 80	1: 90	1: 90	1	1: 130	1: 140	1: 160	1	1: 120	1: 130	1: 150	1

phenylmethane against the Gram-negative, but it is somewhat more effective against the Gram-positive germs. The 3-chloro-2-hydroxydiphenylmethane in which the halogen is in ortho-position to the hydroxyl group is considerably less effective than the corresponding 5-chloro derivative, *i. e.*, one in which the chlorine and the hydroxyl groups are in para-position to each other. The germicidal superiority of the para- over the ortho-halogen substituted compounds has been observed previously in the case of simple phenol derivatives,[4] both *p*-chloro- and *p*-bromophenol being more effectively bactericidal for *E. typhi* and *Staph. pyog. aureus* than the corresponding ortho derivatives.

Little regularity is discernible in the antibacterial behavior of the dihalogen derivatives. They also appear to be strong germicides; however, in one instance no definite bacteriological data could be obtained, in some others the results will be of a somewhat limited significance as the relative insolubility of these compounds necessitated the use of comparatively large quantities of alcohol in the preparation of dilutions; the presence of alcohol in excessive proportions, as will be shown later, may affect the outcome of the experiment either by impairing or by promoting the antibacterial action of the solutions.

The introduction of alkyl groups into the nucleus of phenol and of simple phenol homologs is known to produce an increase of bactericidal potency. The presence of alkyl groups in the compounds of considerable molecular weight under discussion produces no uniform effect on the bactericidal action. The presence of one or two methyl groups increases the germicidal potency against staphylococci and streptococci, the dimethyl derivatives in particular showing extraordinarily high phenol coefficients. The presence of one methyl and one isopropyl group, however, does not have any such effect, the compound in question (5-chloro-6-methyl-3-isopropyl-2-hydroxydiphenylmethane) actually being the least effective in the series. The bactericidal action upon the typhoid and paradysentery germs generally is not intensified by the presence of alkyl groups in the nucleus bearing the hydroxyl group.

In order to obtain an idea of the effect of temperature several chloro derivatives were allowed to act upon *Staph. aureus* at 20°. Table II shows

TABLE II

GERMICIDAL ACTION UPON *Staph. Aureus* AT 20°

Derivatives of hydroxydiphenylmethane	5 min.	10 min.	15 min.	Phenol coeff.
5-Chloro-2-	1:10,000	1:10,000	1:12,000	200
4'-Chloro-4-	1:10,000	1:10,000	1:11,000	195
5-Chloro-4[6]-methyl-2-	1:20,000	1:20,000	1:20,000	380
5-Chloro-4,6-dimethyl-2-	1:40,000	1:40,000	1:40,000	810

[4] Klarmann, Shternov and Von Wowern, *J. Bact.*, 17, 423 (1929).

that somewhat higher concentrations are necessary at the lower temperature to produce a germicidal effect; the numerical values of the phenol coefficients compare with those obtained at 37°.

(b) **Bacteriostatic Effects.**—The data given in Table I indicate the germ-killing action of the compounds prepared. To supplement our knowledge of the antibacterial behavior of this class of chemicals we determined the inhibitory effect of a selected number of them upon the growth of *Staphylococcus aureus*. With this we combined the determination of the status of viability of the germs after different times of exposure to the inhibitory concentrations, ascertaining thereby the concentrations and times at which the bacteria are still capable of development when brought under favorable conditions. In Table III we give a complete record of data obtained with 5-chloro-4,6-dimethyl-2-hydroxydiphenylmethane in order to illustrate the procedure.

This table shows that the growth of staphylococcus in nutrient broth is prevented by a concentration of 1:150,000 or 0.00066% of 5-chloro-4,-6-dimethyl-2-hydroxydiphenylmethane. This result is apparent after twenty-four hours of incubation, and does not change on keeping the set of culture tubes at 37° for another two days. Nevertheless the microbes are not actually dead or incapable of growth for many hours after having been implanted in broth containing this or even stronger concentrations of the compound.

When a transfer to fresh media is made fifteen minutes after planting, the concentration of 1:40,000 appears to be actually germicidal, while one of 1:50,000 is not. The longer the time allowed to elapse between planting and transfer, the lower is the concentration which kills the bacteria. But even after long exposure to the minimum bacteriostatic concentration of 1:150,000. there seem to be individual organisms which when transferred to fresh media are capable of producing growth.

Thus the minimum bacteriostatic concentration for *Staphylococcus aureus* is about twice lower than the minimum bactericidal concentration (given in Table I). It is also noteworthy that by this method the minimum bactericidal concentration after fifteen minutes appears to be 1:40,000, while by the direct method a concentration of only 1:80,000 was found. Indubitably this is due to the presence in the broth of organic matter in the bacteriostatic test, which interferes with the antibacterial action of the chemical.

Similar tests were carried out with a series of four compounds, *viz.*, 5-chloro-2-hydroxydiphenylmethane, 4′-chloro-4-hydroxydiphenylmethane, 5-chloro-4[6]-methyl-2-hydroxydiphenylmethane and 5-chloro-4,6-dimethyl-2-hydroxydiphenylmethane. In Table IV, instead of the complete records only the minimum concentrations are given at which no growth has occurred, and the phenol coefficients of bacteriostatic action.

TABLE III

BACTERIOSTATIC ACTION OF 5-CHLORO-4,6-DIMETHYL-2-HYDROXYDIPHENYLMETHANE

	Time in hours				Transfer to fresh media after							
	24	48	72	96	15 min.	1 hr.	2 hrs.	4 hrs.	6 hrs.	24 hrs.	48 hrs.	72 hrs.
1:40,000	−	−	−	−	−	−	−	−	−	−	−	−
1:50,000	−	−	−	−	+	−	−	−	−	−	−	−
1:60,000	−	−	−	−	+	−	−	−	−	−	−	−
1:70,000	−	−	−	−	+	+	+	−	−	−	−	−
1:80,000	−	−	−	−	+	+	+	+	−	−	−	−
1:100,000	−	−	−	−	+	+	+	+	+	−	−	−
1:150,000	−	−	−	−	+	+	+	+	+	+	−	−
1:200,000	−	+	+	+	+	+	+	+	+	+	+	+
1:250,000	−	+	+	+	+	+	+	+	+	+	+	+
1:300,000	+	+	+	+	+	+	+	+	+	+	+	+
1:400,000	+	+	+	+	+	+	+	+	+	+	+	+
1:500,000	+	+	+	+	+	+	+	+	+	+	+	+

TABLE IV

BACTERIOSTATIC ACTION UPON *Staphylococcus Aureus*

Derivatives of hydroxydiphenylmethane	Minimum inhibitory concentration (96 hrs.)	No growth in subcultures from the following concentrations after						Bacteriostatic phenol coefficient
		15 min.	1 hr.	6 hrs.	24 hrs.	48 hrs.	72 hrs.	
5-Chloro-2-	1: 70,000	1: 7,000	1:15,000	1:20,000	1: 30,000	1: 50,000	1: 70,000	230
4′-Chloro-4-	1: 50,000	1:10,000	1:15,000	1:20,000	1: 20,000	1: 30,000	1: 50,000	165
5-Chloro-4[6]-methyl-2-	1:100,000	1:30,000	1:30,000	1:50,000	1: 70,000	1:100,000	1:100,000	330
5-Chloro-4,6-dimethyl-2-	1:150,000	1:40,000	1:60,000	1:80,000	1:100,000	1:150,000	1:150,000	500
Brilliant green	1:2,000,000	1: 5,000	1:50,000	.....	1:2,000,000	1:2,000,000	1:2,000,000	6600
Phenol	1:300	1:100	1:120	1:150	1:200	1:200	1:300	1

Table IV indicates that the bacteriostatic action upon *Staph. aureus* of the four compounds tested is symbat with their bactericidal action upon the same microörganism. Thus in both cases the presence of the halogen in the nucleus bearing the hydroxyl group makes a more effective bacteriostatic agent than its presence in the other nucleus. The presence of one methyl radical increases the inhibitory capacity while the second methyl group brings about a further increase to more than double the value of the non-alkylated compound.

A parallel test with brilliant green (tetraethyldiaminotriphenylmethane) was included in order to demonstrate that the compounds of the class under discussion are typical bactericidal rather than typical bacteriostatic agents. Thus in three cases the maximum bacteriostatic dilution is only three to five times greater than the bactericidal (in fifteen minutes), while in one case it is ten times greater. In contrast to this, the maximum inhibitory dilution of brilliant green is about four hundred times its maximum germicidal dilution (in fifteen minutes), *i. e.*, the divergence of bactericidal and bacteriostatic concentrations is very considerable; brilliant green is a typical bacteriostatic agent.

The interesting antibacterial properties of the compounds described in this communication have suggested an extension of our investigations to include the alkyl and other alpharyl derivatives of halogenated phenols, work on which is in progress at this time.

Experimental Part

(a) **Chemical.**—The two methods used in the preparation of the compounds under consideration are illustrated in the following two examples.

Method I. Preparation of 3-Chloro-4-hydroxydiphenylmethane, $Cl(3)OH(4)-C_6H_3CH_2C_6H_5$.—*o*-Chlorophenol (51.4 g.) is mixed with 50.6 g. of benzyl chloride and 10 g. of anhydrous zinc chloride is added. The mixture is heated with stirring to 60° and kept at this temperature for two hours, then the temperature is raised to 90° and heating discontinued. Water is added and the mixture shaken with ether. The aqueous portion is withdrawn and the ethereal solution washed with dilute hydrochloric acid and finally with water. The ethereal solution is then shaken repeatedly with dilute potassium hydroxide. The alkaline extracts are washed with ether, then combined and acidified with hydrochloric acid. An oil precipitates which is shaken out with ether, and washed free from acid and salt. After drying and evaporation of the solvent, the oil is subjected to repeated distillation *in vacuo*. The fraction distilling at 155–160° at 5 mm. is isolated.

Besides zinc chloride, aluminum chloride and sulfuric acid were used as condensing agents with success in several instances.

Method II. (Claisen's Reaction) Preparation of 3-Chloro-2-hydroxydiphenylmethane, $Cl(3)OH(2)C_6H_3CH_2C_6H_5$.—*o*-Chlorophenol (128 g.) is dissolved in 500 cc. of toluene and added slowly with constant mechanical stirring to 23 g. of "bird-shot" sodium in 100 cc. of toluene. Violence of reaction may be reduced by occasional immersion of the flask in cold water. When all of the sodium has disappeared the mixture is

cooled to room temperature and benzyl chloride is added very slowly with stirring. The reaction is completed by heating slowly in an oil-bath to 110° and maintaining at this temperature for four hours. The solvent and any uncombined phenol and benzyl chloride are removed by steam distillation. To the residue methyl alcoholic alkali is added and the mixture shaken repeatedly with petroleum ether. The alkaline extract is acidified and, after the usual treatment, the oil is purified by vacuum distillation. The fraction distilling at 144° at 4 mm. is isolated.

Satisfactory results were also obtained when the sodium compounds of the halophenols were prepared by means of sodium hydroxide and subsequent drying of the reaction product.

The following Table V gives the physical constants of the compounds studied, together with a statement of the method and of the initial materials used in their preparation.

TABLE V

HALOGEN DERIVATIVES OF HYDROXYDIPHENYLMETHANE

Derivatives of hydroxydiphenylmethane	Initial materials	Chloride	Method of prepn.	M. p., °C.
3-Chloro-4-	*o*-Chlorophenol	Benzyl	I	
3-Bromo-4-	*o*-Bromophenol	Benzyl	I	
3-Chloro-2-	*o*-Chlorophenol	Benzyl	II	
4'-Chloro-4-	Phenol	*p*-Chlorobenzyl	I	85.5
5-Chloro-2-	*p*-Chlorophenol	Benzyl	I, II	48.5
5-Bromo-2-	*p*-Bromophenol	Benzyl	I	
4'-Chloro-2-	Phenol	*p*-Chlorobenzyl	II	61.5
3,4'-Dichloro-4-	*o*-Chlorophenol	*p*-Chlorobenzyl	I	64
3-Chloro-4'-bromo-4-	*o*-Chlorophenol	*p*-Bromobenzyl	I	65
5-Chloro-3-methyl-2-	*o*-Cresol	Chlorine + benzyl	II	55
4'-Chloro-3-methyl-2-	*o*-Cresol	*p*-Chlorobenzyl	II	48
5-Chloro-4[6]-methyl-2-	4-Chloro-*m*-cresol	Benzyl	II	
5-Chloro-4,6-dimethyl-2-	4-Chloro-symm.-xylenol	Benzyl	I, II	68.5
4'-Bromo-4,6-dimethyl-2-	4-Chloro-symm.-xylenol	*p*-Bromobenzyl	I	101.5
5-Chloro-3-isopropyl-6-methyl-2-	4-Chlorothymol	Benzyl	I	

Formula	B. p., °C.	Mm.	% Halogen Calcd.	% Halogen Found
$Cl(3)OH(4)C_6H_3\cdot CH_2\cdot C_6H_5$	155–160	5	16.22	15.83
$Br(3)OH(4)C_6H_3\cdot CH_2\cdot C_6H_5$	152–154	3	30.38	30.40
$Cl(3)OH(2)C_6H_3\cdot CH_2\cdot C_6H_5$	144	4	16.22	15.64
$OH(4)C_6H_4\cdot CH_2\cdot C_6H_4Cl(4')$	175–177	4	16.22	16.10
$Cl(5)OH(2)C_6H_3\cdot CH_2\cdot C_6H_5$	160–162	3.5	16.22	16.25
$Br(5)OH(2)C_6H_3\cdot CH_2\cdot C_6H_5$	189–192	3.5	30.38	30.42
$OH(2)C_6H_4\cdot CH_2\cdot C_6H_4Cl(4')$	168–171	4	16.22	16.24
$Cl(3)OH(4)C_6H_3\cdot CH_2\ C_6H_4Cl(4')$	160–164	3	28.02	27.62
$Cl(3)OH(4)C_6H_3\cdot CH_2\cdot C_6H_4Br(4')$	182	3	38.79	38.35
$Cl(5)CH_3(3)OH(2)C_6H_2\cdot CH_2\cdot C_6H_5$	147–149	4.5	15.24	14.82
$CH_3(3)OH(2)C_6H_3\cdot CH_2\cdot C_6H_4Cl(4')$	167–172	4	15.24	14.98
$Cl(5)CH_3(4[6])OH(2)C_6H_2\cdot CH_2\cdot C_6H_5$	176–178	4.5	14.38	14.86
$Cl(5)CH_3(4)CH_3(6)OH(2)C_6H\cdot CH_2\cdot C_6H_5$	182–185	4	14.38	14.80
$CH_3(4)CH_3(6)OH(2)C_6H_2\cdot CH_2C_6H_4Br(4')$	194–196	4	27.46	26.98
$Cl(5)C_3H_7(3)CH_3(6)OH(2)C_6H\cdot CH_2\cdot C_6H_5$	175	3	12.91	12.89

The procedure described by Huston and Eldridge[5] was followed in the preparation of 3,5-dichloro-2-hydroxydiphenylmethane. However, the compound was found to melt at 81° while these authors report a melting point of 77–77.5°.

3-Methyl-5-chloro-2-hydroxydiphenylmethane was obtained by chlorination with chlorine in carbon tetrachloride of the condensation product of the sodium compound of *o*-cresol with benzyl chloride, referred to in the papers of Schorigin[6] and of Huston, Swartout and Wardwell.[7]

(b) **Bacteriological.**—The determination of the bactericidal action upon *E. typhi* and *Staph. aureus* was carried out according to the method used by the Food and Drug Administration of the U. S. Department of Agriculture.[8] In the work with *E. paradysenteriae* the same methods of culturing and testing were used as with *E. typhi*. Streptococcus (a very resistant hemolytic strain) was grown for the test in meat infusion–peptone broth (glucose free) at a P_H 7.2–7.4; for subcultures beef extract broth containing 1% of glucose and adjusted to the same P_H was used.

In the preparation of solutions, varying proportions of alcohol were employed. Because of the efficacy of most of the compounds studied toward staphylococci and streptococci in extremely low concentrations, the antibacterial effect of the alcohol present may be regarded as negligible. In most cases the minimum germicidal concentrations for the cocci in Table I did not contain more than 3% of alcohol, with the following exceptions: the extremely insoluble 3,5-dichloro-2-hydroxydiphenylmethane called for 20 and 10% of alcohol, respectively, and 6-methyl-3-isopropyl-5-chloro-2-hydroxydiphenylmethane required 15% of alcohol in both cases. Larger proportions of alcohol were necessary in the tests with the Gram-negative *E. typhi* and *E. paradysenteriae* because of the higher concentrations employed against these more resistant germs than against the Gram-positive cocci. Accordingly in the tests with monohalogen (non-alkylated) derivatives the minimum germicidal concentrations required not more than 5% of alcohol, in those with the alkyl derivatives not more than 15% (except the 6-methyl-3-isopropyl derivative which called for 20%) while the greatest proportion of alcohol had to be used with the dihalogen derivatives: 3,5-dichloro-2-hydroxydiphenylmethane (20%), 3-chloro-4′-bromo-4-hydroxydiphenylmethane (15%) and 3,4′-dichloro-4-hydroxydiphenylmethane (18% in the test with *E. typhi*, but only 3% with *E. paradysenteriae*).

It was considered important, therefore, to attempt a more complete determination of the effect of alcohol in our experiments. It may be assumed that the addition of a small amount of alcohol, by improving the

[5] Huston and Eldridge, THIS JOURNAL, **53**, 2263 (1931).

[6] Schorigin, *Ber.*, **58B**, 2033 (1925).

[7] Huston, Swartout and Wardwell, THIS JOURNAL, **52**, 4488 (1930).

[8] G. L. A. Ruehle and C. M. Brewer, U. S. Dept. of Agriculture, Circular No. 198, Dec., 1931.

solubility of an antiseptic substance, will make the preparation of a concentration within the bactericidal range possible. On the other hand, a large proportion of alcohol may produce one of two effects: a sufficient alcohol concentration may be present to be germicidal *per se*, or the alcohol concentration may be insufficient to kill bacteria, but sufficient to reduce the effectiveness of the antiseptic substance through a shift of its distribution ratio in favor of the aqueous phase. The following experiments, therefore, were made to ascertain to what extent these assumptions were correct.

Although the antibacterial action of alcohol has been studied by previous investigators,[9] it was deemed necessary to carry out an experiment with alcohol under the exact conditions obtaining in our regular tests. The following table illustrates the results.

TABLE VI

BACTERICIDAL ACTION OF ALCOHOL

	5 min.		10 min.		10 min.	
	Killed	Not killed	Killed	Not killed	Killed	Not killed
Staph. aureus	40 (34.5)	30 (25.9)	40 (34.5)	30 (25.9)	40 (34.5)	30 (25.9)
Streptococcus (haemol.)	40 (34.5)	30 (25.9)	40 (34.5)	30 (25.9)	30 (25.9)	25 (21.6)
E. typhi	25 (21.6)	20 (17.3)	20 (17.3)	15 (13.0)	20 (17.3)	15 (13.0)
E. paradysenteriae	25 (21.6)	20 (17.3)	20 (17.3)	15 (13.0)	20 (17.3)	15 (13.0)

The figures without brackets give the alcohol concentrations in per cent. obtained by diluting 95% alcohol. The bracketed figures have been recalculated on the basis of the fact that the addition of 0.5 cc. of culture to 5 cc. of diluted alcohol brings about a further dilution of the latter; they represent the actual concentrations of alcohol (100%) in which the bacteria are suspended. It appears that *E. typhi* and *E. paradysenteriae* are considerably more sensitive to alcohol than staphylococcus and streptococcus. The germicidal alcohol concentrations for the latter two microorganisms appear to be considerably above the alcohol concentrations used in the tests with the antiseptic substances while with *E. typhi* and *E. paradysenteriae* some alcohol concentrations approach those employed in a few tests with the most insoluble antiseptics; thus in certain isolated instances an interfering influence of the alcohol may be counted with.

Another experiment therefore was run in which the dilutions of an antiseptic (5-chloro-2-hydroxydiphenylmethane) were made with diluted alcohol of different concentrations instead of water. The microörganisms used were *E. typhi* and *Staph. aureus*. The results obtained are given in Table VII.

This table shows the interesting fact that alcohol, if used in concentrations which by themselves are not germicidal, is capable of reducing the germicidal action of an antiseptic substance to a considerable extent

[9] F. W. Tilley and J. M. Schaffer, *J. Agr. Res.*, **65**, 611 (1931).

TABLE VII

THE EFFECT OF DILUTED ALCOHOL ON THE BACTERICIDAL POTENCY OF 5-CHLORO-2-HYDROXYDIPHENYLMETHANE

Alcohol concn., %	*Staph. aureus* Minimum germicidal concn. in 5 min.	10 min.	15 min.	*E. typhi* Minimum germicidal concn. in 5 min.	10 min.	15 min.
< 5	1:14,000	1:15,000	1:16,000	1:6500	1:1000	1:7000
10	1:12,000	1:13,000	1:13,000	1:6500	1:6500	1:7000
15				1:8000	1:8000	1:9000
20	1:8000	1:10,000	1:10,000	Indefinite, about 1:60,000		
30	1:6000	1:1000	1:10,000	All dilutions germicidal		
40	All dilutions germicidal			All dilutions germicidal		

(particularly in the case of *Staph. aureus*), the intensity of the impairment depending upon the alcohol concentrations. The most probable reason for this is the shift of the partition equilibrium of the antiseptic substance between the microörganisms and the aqueous-alcoholic phase, in favor of the latter, owing to an increased solvent capacity for the antiseptic substance.

One finds occasionally in the literature that difficultly soluble phenols are brought into solution for the purpose of bacteriological tests by means of diluted alkalies. We ran a series of experiments with three compounds which permitted the preparation of such solutions, using 0.035% potassium hydroxide for the preparation of the initial 0.1% solutions; the further dilutions were made with water. The results given in Table VIII were obtained.

TABLE VIII

THE EFFECT OF ALKALI USED IN THE PREPARATION OF THE INITIAL SOLUTION UPON THE GERMICIDAL ACTION

Derivatives of hydroxydiphenylmethane	*Staph. aureus* 5 min.	10 min.	15 min.	Diff. of effectiveness, %	*E. typhi* 5 min.	10 min.	15 min.	Diff. of effectiveness, %
3-Chloro-4-	1:6,000	1:8,500	1:9,000	−18	1:5,000	1:5,000	1:5,500	0
3-Bromo-4-	1:11,000	1:11,000	1:12,000	−20	1:2,000	1:2,500	1:2,500	−15
5-Chloro-2-	1:14,000	1:16,000	1:18,000	− 2	1:11,000	1:12,000	1:12,000	+ 9

This table indicates that the use of very diluted alkali in preparing solutions offers no advantage, as it produces no uniform effect. It also obscures the picture because of the change of P_H to which bacteria are known to be sensitive in varying degrees.

The determination of the bacteriostatic effect upon *Staphylococcus aureus* was carried out according to the following procedure. To nine cc. of broth (of the same composition as used in growing the germs for the tests on bactericidal action), one cc. of the antiseptic solution was added (containing ten times the concentration which appears in the table). A spiral loop (of five turns of 2.18 mm. inside diameter, wire gage 23 B. and S., and holding approximately 0.02 cc.) was used to plant the twenty-four hour

culture in this mixture previously warmed to 37°. The tubes were kept in the incubator for ninety-six hours. Transfers were made into fresh broth after fifteen minutes, 1, 2, 4, 6, 24, 48 and 72 hours with a loop of the same size. Readings of subcultures were made after forty-eight hours' incubation.

Our thanks are due to Mr. A. Grawehr of our laboratory staff, for valuable assistance rendered in the bacteriological phase of this work.

Summary

A number of mono- and di-halogen derivatives of 2- and of 4-hydroxydiphenylmethanes and their alkyl homologs have been synthesized, either by direct benzylation of halogen phenols or by halogenation of benzylated phenols. The benzyl group was directed into either the ortho or para position to the hydroxyl group by the choice of suitable condensing agents.

While all the compounds of this series were found to be potent bactericides, some derivatives showed an extraordinarily high efficacy toward the two Gram-positive cocci studied (*Staph. aureus* and *Streptococcus haemol.*). Certain regularities in the relation between the antibacterial action and the chemical composition of the compounds studied were found. Thus halogen in the para position to the hydroxyl group conditioned a greater antibacterial efficiency than halogen in ortho position. The 4'-chloro-2-hydroxydiphenylmethane was more effective than the 4'-chloro-4-hydroxydiphenylmethane against the Gram-positive cocci but less so against the two Gram-negative bacteria (*E. typhi* and *E. paradysenteriae*). The monobromo derivatives of both the 2- and the 4-hydroxydiphenylmethanes were less effective than the corresponding monochloro derivatives against the germs of typhoid and paradysentery but more so against staphylococcus and streptococcus. The dihalogen derivatives were also highly bactericidal.

The presence of one or two methyl groups was found to cause a considerable increase in germicidal potency toward the cocci but not toward the germs of typhoid and paradysentery. A methyl and an isopropyl group however, reduce the bactericidal action upon all four microörganisms.

Experiments were also carried out with several compounds to determine their capacity of inhibiting bacterial growth. While, as was to be expected, much lower concentrations were necessary to produce this effect, than to kill the microörganisms upon short exposure, this class of substances appears to show a typically bactericidal rather than a bacteriostatic behavior, when compared, *e. g.*, with bacteriostatic dyes.

Some attention was devoted also to the effect of alcohol used in the preparation of the solutions employed in the bacteriological tests. It was found that alcohol concentrations not germicidal *per se* impaired the antibacterial action of 5-chloro-2-hydroxydiphenylmethane; an explanation

for this was suggested on the basis of an assumed shift of the partition equilibrium of the dissolved substance between the bacteria and the aqueous-alcoholic phase. The effect of diluted alkali in the preparation of the solutions upon their germicidal action was also studied.

BLOOMFIELD, NEW JERSEY

[CONTRIBUTION NO. 93 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

STUDIES IN THE PHENANTHRENE SERIES. II. PHENANTHRENE CARBOXYLIC ACIDS AND 9-BROMOPHENANTHRENE DERIVATIVES[1]

BY ERICH MOSETTIG AND JACOB VAN DE KAMP

RECEIVED APRIL 1, 1932 PUBLISHED AUGUST 5, 1932

These investigations have been carried out in order to find a practicable way of preparing the phenanthrene carboxylic acids, whereby an adequate supply of starting material for further syntheses in this series would be assured.

Of the hitherto known preparative methods, that of Pschorr[2] is the best for the phenanthrene-9-carboxylic acid, while the -2- and -3-carboxylic acids were best prepared through the corresponding phenanthrene-2- and 3-sulfonic acids.[3,4] Neither of these methods is suitable however for large scale preparation of the carboxylic acids.

Recently, Mosettig and van de Kamp[5] found a way of preparing phenanthrene-2- and -3-carboxylic acids by oxidizing 2- and 3-acetylphenanthrenes, respectively, with sodium hypochlorite, a method which seemed much simpler than those hitherto employed because of the relatively easy separation of the acetylphenanthrenes on a large scale and the good yields obtained in their oxidation.

Liebermann and Zsuffa[6] described the preparation of a phenanthrene carboxylic acid from phenanthrene with oxalyl chloride and aluminum chloride. These authors claimed for their acid the constitution of phenanthrene-9-carboxylic acid and mentioned that besides this acid another one, containing the carboxyl group "in the nucleus," was found in smaller quantities.

In consideration of the results which we obtained from the acetylation of phenanthrene,[5] where it was shown that the acetyl group enters the

[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

[2] Pschorr, *Ber.*, **29**, 496 (1896).

[3] Werner and co-workers, *Ann.*, **321**, 248 (1902).

[4] Fieser, THIS JOURNAL, **51**, 2460 (1929).

[5] Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

[6] Liebermann and Zsuffa, *Ber.*, **44**, 207 (1911).

phenanthrene nucleus in the 2- and 3-positions, but not in any detectable degree in the 9-position, it seemed desirable to test Liebermann's results.

When phenanthrene was treated with oxalyl chloride in the presence of aluminum chloride in carbon disulfide solution, under certain conditions a mixture of phenanthrene-3-, -2- and -9-carboxylic acids was formed in an approximate ratio of 75:18:4. Besides these acids, an acid which might be a phenanthrene monocarboxylic acid was formed, whose structure has not as yet been determined because of the small amount obtained (yield about 2%). This acid was compared with a sample of the phenanthrene-1-carboxylic acid[7] which Dr. L. F. Fieser kindly sent us for comparison. No agreement in properties was found, so the formula of the 1-carboxylic acid for our acid is excluded.

These facts are to some extent in accord with the results of the action of acetyl chloride on phenanthrene, where the 3-position is favored, and the 2-position is the next in order of preference. We may remark that nitrobenzene, which gave such good results in the acetylation of phenanthrene, did not prove to be so useful in the case of oxalyl chloride, apparently because of the fact that in this medium we could not run the reaction at the desired low temperature (−15°). Unfortunately it appeared that this interesting formation of the acids was not a practicable method of preparation, first because of the high cost of oxalyl chloride, and second because of the extremely complicated procedure necessary in separating the reaction mixture.

As was shown by Staudinger,[8] oxalyl chloride decomposes in the presence of aluminum chloride into phosgene and carbon monoxide, so that the action of oxalyl chloride on hydrocarbons under these conditions may be considered essentially as the action of phosgene under the catalytic influence of aluminum chloride, whereby the acid chlorides are formed, which in turn are converted into the acids when the reaction mixture is decomposed. Therefore the direct action of phosgene and aluminum chloride on phenanthrene was investigated. The conditions of the experiment were exactly the same as those in the experiment involving oxalyl chloride and phenanthrene, but we did not succeed in isolating any of the expected phenanthrene carboxylic acids.

Phenanthrene, phosgene and aluminum chloride were allowed to react at −15° for twenty-four hours. Not a trace of acid could be isolated from this reaction. The phenanthrene had changed completely. The brown amorphous mass obtained from the reaction mixture could not be crystallized in any way, nor did a high vacuum distillation give a product which could be crystallized.

[7] Prepared from phenanthrene-1-sulfonic acid (private communication from Dr. L. F. Fieser).

[8] Staudinger, *Ber.*, **41**, 3558 (1908).

The action of cyanogen bromide and aluminum chloride, which gave good results with anthracene,[9] gave practically no product in the case of phenanthrene. Under the most varied experimental conditions it was not possible to obtain the expected nitriles. At low temperature and short duration, no reaction took place, whereas with higher temperatures and longer time the phenanthrene was changed completely and only traces of nitrile could be detected (hydrolysis to the carboxylic acids).

It was found, however, that the reaction of Rosenmund,[10] the replacement of nuclear halogen by the cyano group with potassium cyanide in the presence of a cuprous salt as catalyst, could be applied in the phenanthrene series with satisfactory results. We were greatly assisted here by E. I. du Pont de Nemours and Company, Wilmington, Del., who were so kind as to carry out this reaction on a large scale in a high pressure autoclave, and to whom we wish to express our sincere thanks. An even better method, and one requiring no autoclave, was found in the modification of the Rosenmund procedure, recently published by von Braun and Manz.[11] By heating 9-bromophenanthrene with the calculated amount of cuprous cyanide at 260° for six hours, phenanthryl-9-cyanide was obtained in a yield of 90–95% of the theoretical. Because of its simplicity, this method is especially adapted for the production of phenanthrene-9-carboxylic acid in large quantities.

This substitution of nuclear bromine by the cyano group probably can be accomplished also on other bromophenanthrenes, but is of particular advantage for the preparation of phenanthrene-9-carboxylic acid (from the easily accessible 9-bromophenanthrene), which until now has been prepared either by Pschorr's method[12] or through the difficultly obtainable phenanthrene-9-sulfonic acid.[13]

The 9,10-double bond in phenanthrene has a well-marked olefinic character, as is shown in the formation of a 9,10-dibromo addition product[14] and an ether of 10-nitro-9,10-dihydrophenanthrol (-9).[15,16] The polymerization of olefinic compounds which is caused by aluminum halides under certain conditions might account for the unsatisfactory yields of acids or acid chlorides, respectively, in the action of oxalyl chloride on phenanthrene with aluminum chloride. Therefore one might expect that the formation of polymerization products, which appear in the form of unpleasant non-crystallizable and tarry products, would be minimized when the ac-

[9] Karrer and Zeller, *Helv. Chim. Acta*, **2**, 482 (1919).
[10] Rosenmund and Struck, *Ber.*, **52**, 1749 (1919).
[11] Von Braun and Manz, *Ann.*, **488**, 111 (1931).
[12] Pschorr, *Ber.*, **29**, 496 (1896).
[13] Werner, *Ann.*, **321**, 327 (1902); Fieser, Ref. 4; and others.
[14] Hayduck, *Ann.*, **167**, 180 (1873); and others.
[15] Schmidt, *Ber.*, **33**, 3251 (1900).
[16] Wieland and Rahn, *ibid.*, **54**, 1770 (1921).

tivity of the 9,10-double bond is decreased by the introduction of an appropriate substituent, like bromine,[17] in the 9-position. We find, in fact, that when the Friedel–Crafts reaction is carried out on 9-bromophenanthrene with oxalyl chloride or with acetyl chloride[18] in carbon disulfide solution with aluminum chloride, it gives exclusively crystalline compounds.

When oxalyl chloride reacts with 9-bromophenanthrene in carbon disulfide solution under the catalytic influence of aluminum chloride at −15°, the main product formed is a monobromo-monocarboxylic acid of m. p. 283–284°, which appears to be 9-bromophenanthrene-3(or 6)-carboxylic acid. Besides this acid at least two other acids which have not been identified are formed in small quantities. The yield of crystalline material in this reaction is from 90 to 95%. The structure of this monocarboxylic acid was proved by oxidizing its methyl ester with chromic acid in glacial acetic acid solution, whereby a substituted phenanthrene-9,10-quinone was formed, which proved to be identical with the known[19] phenanthrene-9,10-quinone-3-carboxylic acid methyl ester. Furthermore, the bromine atom in the methyl ester of this acid could be replaced by hydrogen, catalyzed with palladium. The reduction resulted in phenanthrene-3-carboxylic acid methyl ester which, as well as the oxidation with chromic acid, shows that the carboxyl group has entered the molecule in the 3- or 6-position.

The reaction between 9-bromophenanthrene and acetyl chloride in carbon disulfide solution in the presence of aluminum chloride at −15° yielded a solid reaction mixture, free from tars and resins, which consisted mainly of 9-bromo-3(or 6)-acetylphenanthrene of melting point 150–151°. The position of the acetyl group was proved by the oxidation of this compound with chromic acid in glacial acetic acid solution, which yielded 3-acetylphenanthrene-9,10-quinone of melting point 217–218.5°, identical with the quinone obtained on oxidation of 3-acetylphenanthrene.[5] The structure could also be demonstrated by oxidation with a 2% sodium hypochlorite solution, which gave an acid which was identical with the 9-bromophenanthrene 3(or 6)-carboxylic acid obtained from 9-bromophenanthrene and oxalyl chloride. Here likewise, besides this main product, at least one other ketone was formed.

The separation and purification of these by-products, as well as of the by-products from the reaction of 9-bromophenanthrene and oxalyl chloride, involved extreme difficulties, however, and were not pursued, and the

[17] *Cf.* Ingold and Ingold, *J. Chem. Soc.*, 2354 (1931).

[18] Although this reaction carried out in nitrobenzene solution on phenanthrene itself gives excellent yields of crystalline products, the same reaction, when run in carbon disulfide solution, leads chiefly to light yellow, heavy oils which could not be crystallized by any means. We hope to collect more experimental material to provide a satisfactory explanation for this remarkable difference in the influence of the solvents.

[19] Fieser, THIS JOURNAL, **51**, 3101 (1929).

question of the position taken by the new substituent (3 or 6) in the main reaction product was likewise left unsettled, since we were mainly interested in showing the quantitative effect of the 9-bromine atom on these two Friedel–Crafts reactions.

Experimental

Phenanthrene with Oxalyl Chloride

Phenanthrene-2-, -3- and -9-Carboxylic Acids.—Twenty-five grams of phenanthrene dissolved in 150 cc. of carbon disulfide in a 500-cc. flask fitted with a mercury-sealed stirrer and a calcium chloride tube was placed in a freezing mixture of ice and salt. Sixty grams of oxalyl chloride was slowly added and to the mixture which was vigorously stirred at −15° was added 12 g. of aluminum chloride in small portions in the course of one-half hour. Immediately after the addition of the aluminum chloride the reaction mixture turned dark green and a rapid stream of hydrogen chloride was liberated. After one-half hour 100 cc. of carbon disulfide and 25 g. of aluminum chloride were added in small portions over a period of forty-five minutes. The evolution of hydrogen chloride which was quite violent in the beginning of the reaction slowed down toward the end, and when the hydrogen chloride had practically ceased to escape (after fourteen hours' stirring at −15°), the dark green viscous reaction mixture was decomposed very cautiously and slowly on cracked ice (under the hood). Violent streams of hydrogen chloride and possibly of phosgene were liberated in the decomposition. The mixture was then treated with 25 cc. of concentrated hydrochloric acid.

In all, 100 g. of phenanthrene was so treated and the decomposed reaction mixtures combined afterward. The carbon disulfide solution of the decomposed reaction mixture had a dark red color. After separating the two layers and removing the carbon disulfide *in vacuo*, a dark brown, sticky, partly solidified residue was obtained. This residue was extracted with 10% sodium carbonate solution until practically no precipitate was obtained on acidifying the filtered alkaline extracts with hydrochloric acid. The precipitate of acids obtained from these extractions will be designated A.

As it appeared that the residue still contained a small amount of an acid in the form of an almost insoluble sodium salt, it was extracted several times by boiling with water. These aqueous extracts were also filtered and acidified and yielded a precipitate of acid, designated B.

The final residue was dissolved in ether and the ethereal solution dried over sodium sulfate. On evaporation of the ether, crystals separated which were filtered and washed with cold ether. After one crystallization from benzene a homogeneous product was obtained, yellow needles melting at 233–234° (uncorr.), yield, 2.0 g. This product, which showed no acid properties, might have been a mono or diketone. The properties and analyses of this compound, however, do not confirm this.

Anal. Subs., 0.0822, 0.0760: CO_2, 0.2618, 0.2421; H_2O, 0.0349, 0.0321. Calcd. for monoketone $C_{14}H_9COC_{14}H_9$: C, 91.06; H, 4.75; for diketone $C_{14}H_9COCOC_{14}H_9$: C, 87.77; H, 4.42. Found: C, 86.86, 86.88; H, 4.75, 4.73.[20]

After this substance had been isolated from the ethereal solution, the latter was evaporated to dryness. Upon standing, the residue crystallized partly to a red cake. From it, by extraction with methyl alcohol, 27 g. of phenanthrene could be recovered, while the remainder consisted of a dark red viscous oil, weighing 16 g., sparingly soluble in most of the common organic solvents, with the exception of pyridine, from which, however, it could not be recrystallized. The investigation of this oil offered little pros-

[20] We did not succeed in the preparation of a quinoxaline derivative which would indicate the presence of an α-diketone.

pect of success and has not been carried further. (If the temperature in this reaction is not kept as low as −15°, the product consists almost entirely of this red oil, and hardly any acid is formed.)

The mixture of acids A consisted of a yellowish-brown flocculent precipitate. In order to purify this precipitate, it was treated with dilute sodium carbonate solution, and the small insoluble residue taken up in ether. The carbonate solution was extracted with ether until the ether came off colorless. The ether extracts contained more of the red oil mentioned above. On acidification of the sodium carbonate solution, a slightly yellow precipitate was obtained which after being filtered, washed with water and dried in air weighed 52 g.

Space does not permit a description of the exact method of working up the mixture of acids, since for the complete separation of the mixture a division into at least sixty fractions was necessary. Neither the solubilities of the acids nor those of their potassium or sodium salts were so different that one component could be easily removed completely. Nevertheless, advantage could be taken of the fact that phenanthrene-3-carboxylic acid is less soluble in xylene, glacial acetic acid or ethyl alcohol than the 2- and 9-isomers. Furthermore, the formation of characteristic micro-crystalline salts enabled us to follow the separation more or less and to identify under the microscope each fraction obtained. Besides these properties, the fact that phenanthrene-9-carboxylic acid methyl ester is much less soluble (and crystallizes much better) than the 2- and 3-isomers, proved to be of great advantage in this separation.

The 52 g. of A was extracted eight times by boiling with 250 cc. of xylene each time. From the last four fractions nearly colorless crystals of phenanthrene-3-carboxylic acid separated, which was purified through its potassium salt. Also the mother liquors of these fractions consisted almost entirely of the 3-acid (melting point 267–269°, melting point of the methyl ester, after one recrystallization, 95–95.5°; mixed melting point with the 3-acid or its methyl ester, obtained on oxidation of 3-acetylphenanthrene[5] 267–269° and 95–95.5°, respectively). The fourth fraction, which had a slight yellow color, also yielded some phenanthrene-3-carboxylic acid. Fractions I, II and III (dark brown) gave only a very small crystalline precipitate of this acid.

The xylene mother liquor of fraction IV was combined with the mother liquors of fractions I, II and III, evaporated to dryness in a vacuum and the remaining residue brought into solution with a little dilute sodium hydroxide solution. With an excess of concentrated sodium hydroxide solution (50%), a very sparingly soluble sodium salt was precipitated which was not homogeneous. Enough water was added therefore to dissolve it again and the mixture of acids was precipitated with hydrochloric acid. After drying, this mixture was esterified with methyl alcohol and concentrated sulfuric acid. In this esterification a resinous product separated out which caused a loss of 5 to 10% of the material. (As yet the cause of this resin formation is unknown. As the original product was entirely alkali-soluble, one may assume that only products of an acid character are present, which, however, can in no way be separated from the phenanthrene-carboxylic acids.)

The brown oily mixture of esters was saponified with a concentrated aqueous sodium hydroxide solution, whereupon the sparingly soluble sodium salt of phenanthrene-2-carboxylic acid separated in shining white leaflets. This salt was uniform and gave, after digesting with hydrochloric acid, pure phenanthrene-2-carboxylic acid, melting point 256–258° (melting point of its methyl ester after one recrystallization from methyl alcohol 95.5–96°; mixed melting points with the 2-acid, or its methyl ester, obtained on oxidation of 2-acetylphenanthrene[5] 257–259° and 95.5–96°, respectively).

From the mother liquors of the sparingly soluble sodium phenanthrene-2-carboxylate the free acids were regenerated; these free acids were put into solution with the calculated

amount of dilute potassium hydroxide and by gradual addition of 50% potassium hydroxide solution, several fractions of potassium salts were precipitated. The first salt fractions consisted of practically pure potassium-3-carboxylate. The last fractions contained a small amount of the 3-acid and a mixture of some other acids, and were dissolved in water again and precipitated with hydrochloric acid. This precipitate was a yellowish-brown crystalline mass and weighed after drying 24 g. It was extracted with hot ethyl alcohol and yielded thus 4 g. of almost white, insoluble crystals. This appeared to be practically pure phenanthrene-3-carboxylic acid, which was further purified through the potassium salt in the usual way. The alcoholic mother liquor was evaporated to dryness and treated with alkali, giving a trace of phenanthrene-3-carboxylic acid in the form of the potassium salt. The remaining mixture was acidified, and the mixture of acids which separated esterified with methyl alcohol and sulfuric acid. A further purification by fractional crystallization of the ester mixture could not be effected. Therefore the mixture of esters was distilled in oil pump vacuum. The slightly yellow distillate was taken up in methyl alcohol, from which a small amount of white needles was deposited. These were collected and after one more distillation in oil pump vacuum melted at 114–115°; a mixed melting point with the methyl ester[5] of phenanthrene-9-carboxylic acid (synthesized according to Pschorr[21]) showed no depression (yield, 1.5 g.).

From the mother liquors of this ester a homogeneous product could not be obtained by fractional crystallization. On saponification of these fractions with sodium hydroxide, a small amount of sodium phenanthrene-2-carboxylate could be collected, whereupon the residual alkaline mother liquors were acidified separately, and from each a yellow mixture of acids was obtained.

Some of these fractions of acid gave a potassium salt crystallizing in shining leaflets, which was purified by two recrystallizations from water. On acidification of its colorless aqueous solution a yellow oil precipitated which upon cooling solidified to yellow needles. After drying in a desiccator, the melting point of the acid was found to be between 70 and 75°. Apparently it contained water of crystallization; after drying at 100° in a vacuum and recrystallizing from benzene, the acid melted at 123–125°.[22] It was analyzed in the form of its potassium salt, which was dried at 100° in a vacuum.

Anal. Subs., 0.0586: K_2SO_4, 0.0193. Calcd. for phenanthrene monocarboxylic acid potassium salt $C_{15}H_9O_2K$: K, 15.03. Found: K, 14.78.

The precipitate B consisted of practically pure phenanthrene-2-carboxylic acid, which was purified through its sodium salt; melting point of the acid 258–260°, of the methyl ester 95.5–96°.

Whether acids were formed in the oxalyl chloride reaction which could not be esterified or were unstable under the conditions of separation could not be determined. From the original mixture of 52 g. of acids, 22.5 g. of pure acids was obtained: 17 g. of phenanthrene-3-carboxylic acid, 4 g. of phenanthrene-2-carboxylic acid, 1 g. of phenanthrene-9-carboxylic acid and 0.5 g. of the yellow acid of m. p. 123–125°.

Preparation of Phenanthrene-9-carboxylic Acid from 9-Bromophenanthrene.—A mixture of 50 g. of 9-bromophenanthrene (m. p. 63°), 30 g. of cuprous cyanide, 75 g. of potassium cyanide, 100 cc. of methyl alcohol and 40 cc. of water was heated at 210° for eight hours in an autoclave of 500 cc. capacity. The autoclave was heated in a bath of refluxing nitrobenzene (205–210°). After the autoclave had cooled down to room temperature the excess pressure was released (strong odor of ammonia). The reaction mixture was removed from the autoclave by pouring the liquid part into water

[21] Pschorr, *Ber.*, **29**, 496 (1896).

[22] The phenanthrene-1-carboxylic acid prepared by Dr. L. F. Fieser melts at 232° (private communication).

and washing out the solid crystalline cake with water. After evaporation of the alcohol the mixture was filtered. From the filtrate a small amount (10–15%) of phenanthrene-9-carboxylic acid could be thrown out and purified through its potassium salt. The precipitate on the filter was extracted with ether. After drying and evaporating the ether, the residue was hydrolyzed by boiling with a 25% methyl alcoholic potassium hydroxide solution, which yielded the 9-acid. The acid thus collected combined with the small amount already obtained weighed 36 g. (yield, 83% of the theoretical). Recrystallized from glacial acetic acid, the acid melted at 251–252°.

The following procedure, which does not necessitate the use of an autoclave, was found to be most convenient. Thirty grams of 9-bromophenanthrene was mixed with 12 g. (1 mole + 10%) of finely powdered cuprous cyanide and heated at 260° for six hours. The reaction mixture, which solidified entirely upon cooling to room temperature, was finely powdered and extracted with ethyl alcohol or with chloroform. On evaporation of the solvent and removal of the last traces in a vacuum, 22.1 g. of phenanthryl-9-cyanide was obtained, which after one recrystallization from alcohol melted at 103–104°; yield, 93% of the theoretical. This nitrile was hydrolyzed to phenanthrene-9-carboxylic acid by boiling with 25% methyl alcoholic potassium hydroxide; yield, 90% of the theoretical.

9-Bromophenanthrene with Oxalyl Chloride.—Fifteen grams of 9-bromophenanthrene in 125 cc. of carbon disulfide, 25 cc. of oxalyl chloride, and 25 g. of aluminum chloride were allowed to react in the way described above. After decomposition of the reaction mixture a slightly yellow crystalline mixture of acids resulted which was filtered and brought into solution with dilute alkali. The alkaline solution was extracted with ether to remove unchanged 9-bromophenanthrene, and the acids were precipitated with hydrochloric acid. After drying, 15.5 g. of a mixture of acids was obtained; yield, 85% of the theoretical. (Ten to twelve per cent. of bromophenanthrene was recovered.) In all, 85 g. of 9-bromophenanthrene was so treated. The separation of the mixture of acids was carried out through their methyl esters.

9-Bromophenanthrene-3(or 6)-carboxylic Acid Methyl Ester, $C_{14}H_8BrCOOCH_3$.—Thirty grams of the mixture of acids described above, 600 cc. of methyl alcohol and 45 g. of concentrated sulfuric acid were boiled for four hours. During this esterification, part of the esters crystallized out. The esterification mixture was worked up in the usual way. Because of its slight solubility in methyl alcohol the methyl ester of 9-bromophenanthrene-3(or 6)-carboxylic acid was easily isolated and purified as white needles of m. p. 155–155.5°, sparingly soluble in methyl alcohol and ether, more soluble in glacial acetic acid, dioxane and chloroform.

Anal. Subs., 0.0904, 0.0798: AgI, 0.0657, 0.0577. Calcd. for $C_{16}H_{11}O_2Br$: one methoxyl, 9.83. Found: 9.60, 9.55.

9-Bromophenanthrene-3(or 6)-carboxylic Acid, $C_{14}H_8BrCOOH$.—The ester was saponified to the acid with 25% methyl alcoholic potassium hydroxide; yield, quantitative. The acid is recrystallized from glacial acetic acid, in which it is sparingly soluble, as white needles of m. p. 283–284° (uncorr.).

Anal. Subs., 0.1492: AgBr, 0.0942. Calcd. for $C_{15}H_9BrO_2$: Br, 26.55. Found: Br, 26.87.

This acid forms well-crystallized potassium and sodium salts, which are only sparingly soluble in water.

By treating the 9-bromophenanthrene-3(or 6)-carboxylic acid methyl ester with chromic acid in the usual way, a quinone was obtained which after recrystallization from glacial acetic acid melted at 210–212°. The mixed melting point with phenanthrene-9,10-quinone-3-carboxylic acid methyl ester, obtained from phenanthrene-3-carboxylic acid methyl ester, gave no depression.

Debromination of 9-Bromophenanthrene-3(or 6)-carboxylic Acid Methyl Ester with Hydrogen.—To a suspension of 0.1 g. of palladous hydroxide–calcium carbonate catalyst (Pd content 1%) in a mixture of 3 cc. of ethyl alcohol and 1 cc. of water, 0.1 g. of 9-bromophenanthrene-3(or 6)-carboxylic acid methyl ester dissolved in a mixture of 10 cc. of ethyl alcohol and 5 cc. of pyridine was added under a stream of hydrogen. On shaking the mixture with hydrogen, the calculated absorption was reached in about twenty minutes. Upon filtering the reaction mixture from the palladium–calcium carbonate and pouring the filtrate into 250 cc. of 10% hydrochloric acid, phenanthrene-3-carboxylic acid methyl ester separated practically pure. After one recrystallization from methyl alcohol the melting point is 95–95.5°. A mixed melting point with a sample of ester prepared from 3-acetylphenanthrene showed no depression.

The separation of the mixture of methyl esters contained in the mother liquors of 9-bromophenanthrene-3(or 6)-carboxylic acid methyl ester was attempted by laborious fractional crystallization from several solvents. A uniform product could not be obtained.

9-Bromophenanthrene with Acetyl Chloride

9-Bromo-3(or 6)-acetylphenanthrene, $C_{14}H_8BrCOCH_3$.—Twenty-five grams of 9-bromophenanthrene in 200 cc. of carbon disulfide, 10 g. of acetyl chloride and 40 g. of aluminum chloride were allowed to react in the way described above. After decomposition of the reaction mixture a light yellow oil was obtained, which soon solidified to an almost white crystalline cake. Fractional crystallization of this cake from methyl alcohol yielded mainly 9-bromo-3(or 6)-acetylphenanthrene (±70% yield), besides a small amount of unchanged bromophenanthrene and a mixture of other ketones. The 9-bromo-3(or 6)-acetylphenanthrene was purified by two more recrystallizations from methyl or ethyl alcohol (with animal charcoal), from which solvents it crystallizes in long white needles of m. p. 150–151°. It is easily soluble in dioxane or glacial acetic acid, sparingly soluble in ether, methyl or ethyl alcohol and chloroform.

Anal. Subs., 0.1610: AgBr, 0.1023. Calcd. for $C_{16}H_{11}OBr$: Br, 26.73. Found: Br, 27.04.

9-Bromo-3(or 6)-acetylphenanthrene Semicarbazone.—The semicarbazone which was prepared in the usual way was recrystallized from methyl alcohol in which it is very sparingly soluble; white needles of m. p. 265–265.5° (uncorr.).

Anal. Subs., 0.1351: 14.65 cc. of N (29°, 746 mm.). Calcd. for $C_{17}H_{14}ON_3Br$: N, 11.80. Found: N, 12.03.

9-Bromo-3(or 6)-acetylphenanthrene Oxime.—Recrystallized from methyl alcohol it forms white needles of m. p. 142.5–143° (uncorr.).

Anal. Subs., 0.1541: 6.5 cc. of N (28°, 746 mm.). Calcd. for $C_{16}H_{12}ONBr$: N, 4.46. Found: N, 4.70.

Oxidation with Sodium Hypochlorite.—One gram of 9-bromo-3(or 6)-acetylphenanthrene was oxidized with a 2% sodium hypochlorite solution.[5,23] The acid obtained melted after one recrystallization from glacial acetic acid at 283–284°. A mixed melting point with the 9-bromophenanthrene-3(or 6)-carboxylic acid described above showed no depression; yield, almost quantitative. One-half gram of this acid esterified with methyl alcohol and sulfuric acid yielded a methyl ester of m. p. 155–155.5°. This methyl ester gave no depression in melting point with the methyl ester of 9-bromophenanthrene-3(or 6)-carboxylic acid described above.

Oxidation with Chromic Acid.—The oxidation with chromic acid of 9-bromo-3-(or 6)-acetylphenanthrene was carried out in the usual way. The quinone obtained

[23] Graebe, *Ber.*, **35**, 2753 (1902).

melted after two recrystallizations from glacial acetic acid at 217–218.5°. A mixed melting point with the quinone obtained by oxidation of 3-acetylphenanthrene showed no depression.

Summary

1. The action of oxalyl chloride on phenanthrene described by Liebermann and Zsuffa has been shown to yield not phenanthrene-9-carboxylic acid as the main product, but phenanthrene-3-carboxylic acid, accompanied by smaller quantities of the 2- and 9-isomers and an acid of melting point 123–125° whose structure has not yet been determined.

2. A good preparative method for phenanthrene-9-carboxylic acid is described.

3. The influence of bromine substitution in the 9-position on Friedel–Crafts reactions in this series has been investigated.

4. 9-Bromophenanthrene-3(or 6)-carboxylic acid and 9-bromo-3(or 6)-acetylphenanthrene are described.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

PRODUCTION OF BUTENES BY PYROLYSIS OF THE NORMAL MONOCHLOROBUTANES

BY PAUL E. WESTON[1] AND H. B. HASS

RECEIVED APRIL 4, 1932 PUBLISHED AUGUST 5, 1932

Introduction

In recent years normal butane has become available in large quantities at a low price. It is conceivable that this butane can be converted into more valuable substances through the butenes as intermediates, for example into *sec.*-butyl alcohol, by chlorination of the *n*-butane, splitting off hydrogen chloride from the monochlorobutanes, and hydration of the resulting butenes. In addition to the direct economic importance, this method of producing the butenes is of fundamental importance to the general chemistry of the olefins, for the butenes are the simplest substances in which it is possible to have the shifting of a hydrogen atom from one carbon atom to another (shifting of a double bond), stereomutation between *cis* and *trans* forms and shifting of a methyl group. A survey of the literature has shown that almost no information at all is available concerning the conditions governing these changes.[2] Lucas and his associates[3] have been at-

[1] Research Chemist with the Purdue Research Foundation, J. K. Lilly Research Fellowship.

[2] Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35**, 1825, 1860, 1866 (1931).

[3] Young and Lucas, THIS JOURNAL, **52**, 1964 (1930); Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); Lucas, Dillon and Young, *ibid.*, **52**, 1949 (1930).

tacking this problem through the pyrolysis of the butyl alcohols, while we have been attacking it through the pyrolysis of the monochlorobutanes.

The splitting off of hydrogen halides from ethyl, propyl, isobutyl, isoamyl, hexyl and heptyl halides to form olefins has been accomplished, using pumice, soda lime,[4] bivalent metallic chlorides, and alumina as catalysts. The reactions are reversible, and therefore the hydrogen halide must be removed, or the products cooled quickly, to prevent recombination. The catalysts gradually lose their activity by the formation of a carbonaceous deposit on them.

We have found that the pyrolyses of 1-chlorobutane and 2-chlorobutane in a glass tube are homogeneous vapor phase reactions, 1-chlorobutane giving all 1-butene, and 2-chlorobutane giving a mixture of 1-butene, *cis*-2-butene, and *trans*-2-butene. When calcium chloride was used as a catalyst, 2-chlorobutane gave almost entirely the 2-butenes, and 2-chlorobutane gave very largely 2-butenes also.

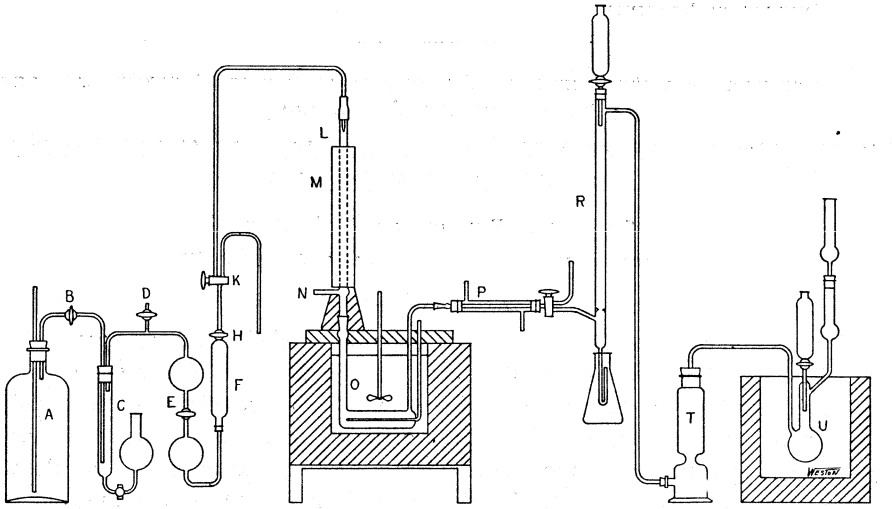


Fig. 1.—Apparatus for studying the pyrolysis of the monochlorobutanes.

Experimental Part

The apparatus is shown in Fig. 1. The parts A to L were designed to obtain a constant rate of flow of chlorobutane. Water from a source having a constant head (about 4.56 meters) flowed into the 2-liter bottle, A, compressing the air to a constant pressure. This air bubbled through mercury in C, and exerted pressure on some very viscous oil in the upper bulb of E. The rate of flow of oil could be adjusted by the stopcock, E. The oil displaced mercury in the lower bulb of E, which in turn displaced the chlorobutane from the graduated 50-ml. separatory funnel, F, into the vaporizer, M. As the mercury rose in F, the back pressure increased, and so to prevent a decrease in the

[4] Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 125; Faragher and Garner, THIS JOURNAL, **43**, 1715 (1921).

rate of flow, the pressure on the oil in E was increased by allowing an equivalent amount of mercury to escape from C. Since the oil had a high viscosity, the opening in the stopcock had to be relatively large, and therefore small solid particles would not block the opening and alter the rate of flow, as would be the case if an attempt were made to control the flow of chlorobutane directly.

The chlorobutane was vaporized in the electrically heated tube, M. Indentations in the walls of the tube caused turbulent flow and better heating. The temperature of the vapor, as it entered the reaction tube, was about 100° as indicated by a thermometer inserted in the opening, N.

The reaction tube, O, of Pyrex glass, was immersed in an electrically heated bath of sodium nitrate and potassium nitrate. The temperature was kept uniform by stirring, and was controlled by a Leeds and Northrup potentiometer controller actuated by a thermocouple immersed in the bath. A well sealed into the reaction tube contained two thermocouples, one at each end. A loosely fitting glass plug placed in the entrance tube, O, caused the vapor to flow close to the hot walls and become heated quickly. The products were cooled quickly to reduce the extent of the reverse reaction by leading them through a capillary into the water cooler, P. The reaction tube could be removed by separating the ground joints.

The extent of reaction was determined by dissolving the hydrogen chloride in standard sodium hydroxide solution as it trickled over glass beads in the tower, R, and titrating the excess alkali. Unreacted chlorobutane which collected with the alkali did not react with it, or interfere with the titration in any way. From the moles of hydrogen chloride evolved and the moles of chlorobutane used, the extent of reaction was calculated. The exposure time, or duration of the reaction, was calculated from the rate of introduction of the chlorobutane, the volume of the reaction tube (53 ml.) and the mean of the entering and leaving volumes of gas, as calculated from the extent of reaction and the gas laws. This of course does not give the true reaction time.

The butenes were analyzed by converting them into the bromides and determining, for the bromides, the densities and reaction rates with potassium iodide in methanol, exactly as described by Dillon, Young and Lucas. The butenes were dried with calcium chloride in the tower, T, liquefied, and allowed to react with bromine in the bath, U, at −15 to −20°. The bromides were distilled under reduced pressure before being analyzed, to remove small amounts of chlorobutanes and butadiene tetrabromide.

Both 1-chlorobutane and 2-chlorobutane were prepared by the thermal chlorination of *n*-butane. Butane and chlorine were used in the ratio of 10:1 by volume, at a reaction temperature of 400–475°. The product consisted of 90.3% monochlorides and 9.7% polychlorides by weight. The monochlorides consisted of 63% 2-chlorobutane and 37% 1-chlorobutane. Unreacted butane was recycled. The chlorides were separated by rectification. The 1-chlorobutane used in this research had a boiling point of 77.6–77.7° at 743 mm., or 78.3–78.4° corrected to 760 mm.[5] The 2-chlorobutane had a boiling point of 67.2–67.3° at 740 mm., or 68.0–68.1° corrected to 760 mm. If the butane used above contained any isobutane, the 2-chlorobutane made from it would have been contaminated with isobutyl chloride; for the boiling points of these isomers are only one degree apart; therefore some 2-chlorobutane was also prepared from the alcohol and hydrochloric acid. This 2-chlorobutane[6] had a boiling point of 67.4° at 743 mm., or 68.0° corrected to 760 mm.

Discussion of the Rate of Reaction

The thermal decompositions of 1-chlorobutane at 550° and 2-chlorobutane at 500° in a glass tube are homogeneous vapor phase reactions.

[5] "International Critical Tables," Vol. III, p. 246.

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. V, 1925, p. 27.

The data to support this conclusion are given in Table I and Fig. 2. The reactions were run under three different conditions, namely, in a clean reaction tube (cleaned by burning the carbonaceous deposit with air), in a tube coated with the carbonaceous deposit which slowly formed from side reactions, and in a tube stuffed with glass wool. All of the points fit the curves equally well, indicating that the glass surface and the carbonaceous deposit did not alter the rate of reaction. In the table, two reaction temperatures are given, the first being the temperature at the entrance and the second at the exit of the reaction tube. Different temperatures were obtained at different rates of flow, and the temperatures inside the tube never equaled the temperature of the bath because these reactions are endothermic. The 2-chlorobutane from the alcohol reacted slightly, but definitely faster than the 2-chlorobutane from chlorination of butane, probably because the latter contained some isobutyl chloride, a primary chloride. It can be seen from the curves that 1-chlorobutane, a primary

TABLE I

RATE OF PYROLYSIS OF THE MONOCHLOROBUTANES (PLOTTED IN FIG. 2)

Expt.	Reaction temp., °C.	Moles BuCl	Moles HCl	Duration of expt., min.	Reaction, %	Exposure, seconds	Chlorobutane	Reaction tube
1	499–9	0.1665	0.0166	31.0	10.0	8.9	1-	Clean
2	547–7	.1020	.0331	12.0	32.4	4.8	1-	Clean
3	548–8	.0956	.0418	18.0	43.7	7.3	1-	Clean
4	548–9	.1160	.0633	33.0	54.5	10.6	1-	Clean
5	546–6	.1870	.0469	15.0	25.1	3.4	1-	Carbonized
6	545–7	.0986	.0398	16.0	40.4	6.4	1-	Carbonized
7	544–4	.1940	.0442	14.0	22.8	3.1	1-	Glass wool
8	547–7	.0977	.0414	17.0	42.4	6.8	1-	Glass wool
9	547–7	.1010	.0484	22.0	48.0	8.3	1-	Glass wool
10	493–7	.0765	.0660	15.0	86.3	6.8	2-	Clean
11	492–8	.0929	.0776	17.0	83.7	6.5	2-	Clean
12	490–5	.1221	.0850	15.0	69.5	4.6	2-	Clean
13	490–5	.1480	.0901	13.0	60.9	3.4	2-	Clean
14	490–5	.1480	.0899	13.0	60.6	3.4	2-	Clean
15	488–92	.1708	.0619	7.0	36.2	1.75	2-	Clean
16	490–3	.1711	.0846	11.0	49.4	2.6	2-	Clean
17	493–9	.0994	.0860	21.0	86.6	7.4	2-	Carbonized
18	491–6	.1141	.0790	13.0	69.1	4.2	2-	Carbonized
19	490–5	.1540	.0835	11.0	54.1	2.8	2-	Carbonized
20	492–6	.1151	.0886	17.0	76.9	5.4	2-	Carbonized
21	490–6	.1022	.0829	15.0	81.0	5.3	2-*ex* alc.	Clean
22	491–5	.1250	.0798	11.0	63.7	3.4	2-*ex* alc.	Clean
23	488–93	.1693	.0785	9.0	46.4	2.2	2-*ex* alc.	Clean
24	490–7	.1200	.0790	11.0	65.9	3.5	2-	Glass wool
25	489–93	.1560	.0777	10.0	49.8	2.4	2-	Glass wool
26	492–8	.1192	.0891	17.0	74.6	5.3	2-	Glass wool
27	489–94	.1095	.0803	13.0	73.1	4.4	2-*ex* alc.	Glass wool
28	492–8	.0976	.0860	19.0	88.0	6.8	2-*ex* alc.	Glass wool

chloride, reacted much more slowly than 2-chlorobutane, a secondary chloride. The amount of carbonaceous deposit which formed was very small, being only about 0.01 g. per 380 g. of chlorobutane decomposed.

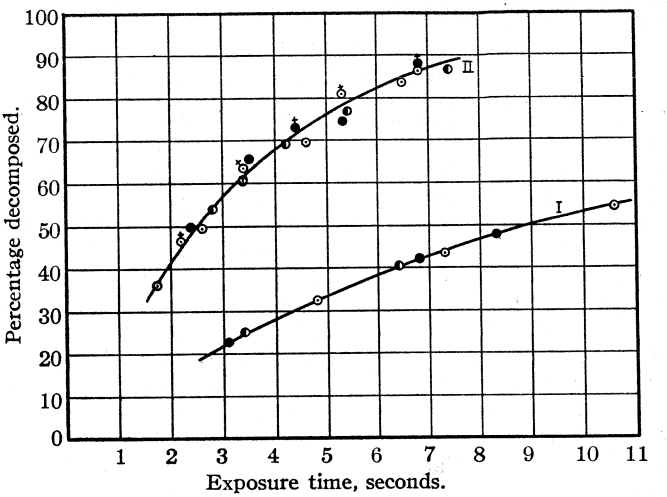


Fig. 2.—Rate of pyrolysis of the monochlorobutanes: I, 1-chlorobutane at 550°; II, 2-chlorobutane at 500°; ⊙, clean reaction tube; ◐, carbonized reaction tube; ●, tube stuffed with glass wool; +, indicates that the 2-chlorobutane was made from the alcohol.

Discussion of the Composition of the Butenes

The compositions of the butenes obtained under various conditions are given in Table II. In the absence of a catalyst at 550°, 1-chlorobutane gave only 1-butene (Expt. 1), but 2-chlorobutane gave a mixture of all three normal butenes (Expt. 3). The butenes from 2-chlorobutane were about two-thirds 2-butenes, and of these, two-thirds was the lower-boiling isomer (*trans*). If the butenes were formed by the simple splitting off of a molecule of hydrogen chloride followed by rearrangement of the radical to a more stable form, it seems obvious that 1-chlorobutane should yield almost entirely 1-butene while 2-chlorobutane should yield a mixture of the isomers. The 1-butene does not rearrange easily under these conditions to 2-butenes, for in Expt. 2 the reaction time allowed was almost twice that in Expt. 1, but still 1-chlorobutane yielded all 1-butene. Under prolonged exposure, some of the 1-butene decomposed into butadiene, and the tetrabromide formed from the butadiene impaired the accuracy of the analysis, but even so, if there was a rearrangement of the 1-butene, it occurred to a very small extent.

The composition of the butenes did not change with the reaction temperature, for at 450, 490, 500 and 550° (Expts. 3 to 10) the mean composi-

tion was 1-butene 35 ± 3%, *cis*-2-butene 22.5 ± 3.5%, and *trans*-2-butene 43 ± 4%, except No. 8, which was 6% low. In all of these experiments the results were the same with 2-chlorobutane prepared either from the alcohol or by chlorination of butane.

TABLE II

COMPOSITION OF BUTENES

Expt.	*t*, °C.	BuCl and source	Reaction time, sec.	Bromides d_{20}	Bromides K_{75}	Butenes, % 1-	Butenes, % *Cis*-2-	Butenes, % *Trans*-2-
1	550	1-	6	1.8028	0.0782	100	..	..
2	550	1-	10	1.8051	.0769	100	..	..
3	550	2-*ex* Cl_2	2	1.7889	.0572	35	20	45
4	500	2-*ex* Cl_2	6	1.7891	.0577	37	19	44
5	500	2-*ex* alc.	6	1.7886	.0558	33	21	46
6	500	2-*ex* Cl_2	6	1.7891	.0555	33	25	42
7	490	2-*ex* Cl_2	..	1.7894	.0555	34	26	39
8	490	2-*ex* Cl_2	..	1.7898	.0564	38	26	37
9	490	2-*ex* Cl_2	..	1.7888	.0557	32	23	45
10	450	2-*ex* Cl_2	11	1.7891	.0576	37	19	44
11	450	1-	Catalyst	1.7893	.0490	22	42	36
12	450	2-*ex* Cl_2	Catalyst	1.7884	.0468	13	44	43
13	450	2-*ex* alc.	Catalyst	1.7888	.0468	16	45	39
14	400	2-*ex* Cl_2	Catalyst	1.7858	.0456	0	35	66
15	250	2-*ex* Cl_2	Catalyst	1.7869	.0458	5	39	56

When anhydrous calcium chloride was used as a catalyst at 450° the butenes produced from both 1-chlorobutane and 2-chlorobutane were largely 2-butenes. Enough catalyst was used to fill the reaction tube entirely and the chlorobutanes were run slowly enough to obtain a high yield of butenes. The catalyst became covered with a dark gray deposit and lost most of its activity in two hours. Only 22% 1-butene was obtained from 1-chlorobutane with the catalyst compared to 100% 1-butene without a catalyst (Expts. 1 and 11), and only 13–16% 1-butene from 2-chlorobutane compared to 33% (Expts. 12, 13). At still lower temperatures, 400 and 250°, 2-chlorobutane gave almost no 1-butene at all when the catalyst was used (Expts. 14, 15). It is unknown whether the butenes rearranged in contact with the catalyst, or whether the catalyst caused the reaction to go in such a way that principally the 2-butenes were formed directly from the chlorobutanes, but Ipatiev and Zdzitovetsky[7] state that zinc chloride does not cause rearrangement of either the *n*-butenes or isobutene. A study of the behavior of these butenes in contact with various catalysts would aid in explaining the results obtained by Dillon, Young and Lucas with the butyl alcohols, as well as these results with the chlorobutanes.

Summary

A study has been made of the thermal decomposition of 1-chlorobutane and 2-chlorobutane in the absence of a catalyst, and using anhydrous

[7] Ipatiev and Zdzitovetsky, *Chem. Abstracts*, **2**, 259 (1908).

calcium chloride as a catalyst. The extent of reaction was determined by titrating the hydrogen chloride evolved, and the mixtures of butenes were analyzed by determining for their bromides, the densities and the reaction rates with potassium iodide in methanol.

In the absence of a catalyst, the decompositions of 1-chlorobutane at 550° and of 2-chlorobutane at 500° are homogeneous gaseous reactions. 1-Chlorobutane gave only 1-butene, but 2-chlorobutane gave a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene. The composition of the product from 2-chlorobutane was the same at 450, 500 and 550°.

In the presence of the catalyst at 450°, both chlorobutanes gave mixtures of all three butenes, there being relatively little 1-butene, however.

It is unknown whether the butenes rearranged in contact with the catalyst, or whether the catalyst caused the reaction to go in such a way that principally the 2-butenes were formed directly from the chlorobutanes.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. X. CONSTITUENTS OF THE RUBBER HYDROCARBON

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

RECEIVED APRIL 6, 1932 PUBLISHED AUGUST 5, 1932

It has been shown in the seventh paper of this series,[1] that nitrogen-free rubber hydrocarbon can be prepared by fractional precipitation of natural rubber from a mixture of alcohol and benzene. This fractionation method is now applied to the rubber hydrocarbon itself to determine whether it is a single individual or a mixture of various components, and, in the last event, to isolate these constituents.

Some criterion is needed to follow the progress of any fractionation. The measurement of a well-defined physical property is best. In the present research, use is made of a standardized precipitation point (abbreviated to s. p. p. in the text), which is defined as follows. The standard precipitation point of a rubber specimen is the temperature at which a sudden increase of turbidity occurs in a slowly cooled solution of 0.85% rubber, 28.55% absolute alcohol and 70.60% benzene. The manner in which the s. p. p. is determined is described in the experimental part of this paper.

Procedure

Two hundred and fifty grams of crepe rubber was dissolved in benzene and fractioned into primary cuts. The method of fractionation was a duplication of that reported in the seventh paper. The technique, however, was improved to prevent alteration of the specimen by light or oxygen. The flasks containing the rubber solu-

[1] Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).

tions were always completely covered with black cloth, frequently evacuated and filled with carbon dioxide. The solvents were removed by suction at room temperature. The rubber samples were stored in a bed of solid carbon dioxide. They were allowed to reach room temperature and exposed to atmospheric oxygen only during the short time required to take a sample for s. p. p. determinations.

Table I reports the results of this primary fractionation.

TABLE I

PRIMARY FRACTIONATION OF 250 G. OF CREPE RUBBER

Fractions	Amount, g.	Standard precipitation point (s. p. p.)	% based on 233.6 g.	
A_1	44.8	33.0°	19.2	
A_2	38.8	33.0°	16.6	
A_3	46.5	34.9°	19.9	81.5%
A_4	28.2	35.0°	12.1	
A_5	31.9	35.3°	13.7	
B	43.4	Not obtained	18.6	
Total	233.6		100.1%	
Loss	16.4			

The loss of rubber during this separation amounts to 6.6% of the original 250-g. sample. This 16.4-g. loss includes an estimated amount of 12.5 g. of so-called "resins."

The tabulated results are shown on the chart, where the percentages are plotted against the s. p. p. They are represented by the solid line: the length of the horizontal lines measures the size of the fractions from

TABLE II

SECONDARY FRACTIONATION OF FRACTIONS A_1 TO A_5, *viz.*, 81.6% OF THE RUBBER HYDROCARBON

Fractions	Amounts, g.	S. p. p.	% based on 190.2 g. = 81.5%
A_1 Top[a]	11.0	32.1	5.4
Bottom[a]	29.8	34.2	14.7
A_2 Top	9.8	32.5	4.8
Bottom	24.2	34.2	11.9
A_3 Top	6.7	31.2	3.3
Bottom	30.7	34.8	15.1
A_4 Top	4.2	31.2	2.1
Bottom	19.7	35.0	9.7
A_5 Top	3.8	31.5	1.9
Bottom	25.7	35.1	12.6
Total	165.6		81.5
Loss	24.6		

The losses are almost entirely due to sampling for s. p. p. determinations.

[a] "Bottom" is the rubber which settles out from a benzene–alcohol mixture held at 1° below its precipitation point. "Top" is the rubber chilled out from the supernatant liquid.

A_1 to A_5, in percentage of recovered rubber. Fraction B could not be shown on the chart since its s. p. p. could not be determined. It amounted to 18.6% of the total, and consequently the curve on the chart stops short of 100% by this amount, *viz.*, at 81.4%.

Each of the primary cuts, from A_1 to A_5 inclusive, amounting to 81.5% of the rubber recovered, was then resubjected to the same fractionation method. The only experimental detail altered was the lengthening of the time allowed for complete separation to fourteen hours. The results are given in Table II. These results appear on the chart.

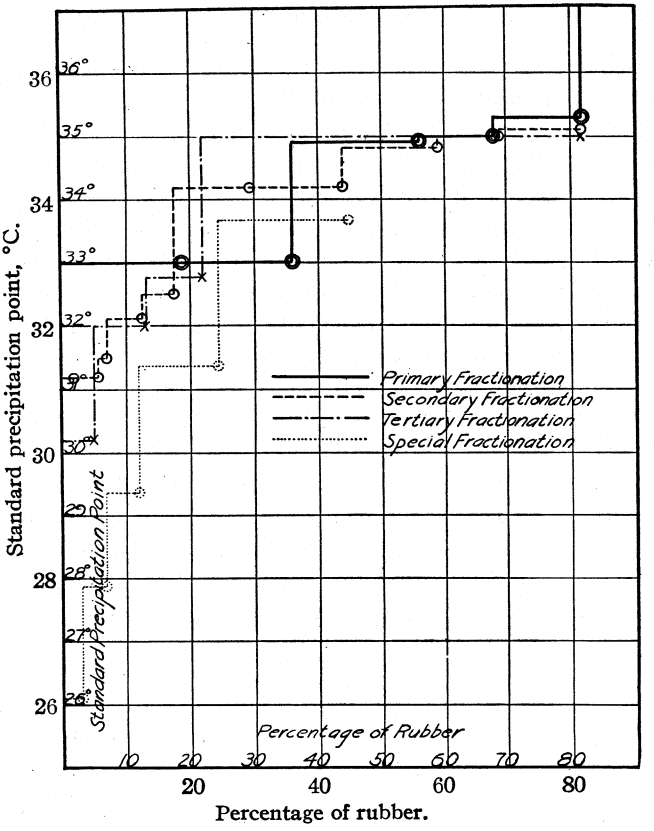


Fig. 1.

A third fractionation was then accomplished as follows. Cuts with an s. p. p. lower than 33° were put together, while cuts with an s. p. p. higher than 33° were united. The two fractions thus formed were separately fractioned as for the secondary fractionation, and the results shown in Table III were obtained. These results appear on the chart.

The third fractionation is only slightly better than the second one.

TABLE III

TERTIARY FRACTIONATION OF FRACTIONS A_1 TO A_5, OR 81.6% OF RUBBER HYDROCARBON

Fractions		Amounts, g.	S. p. p.	% based on 190.2 g. = 81.5%
Sum of tops	Top	8.5	30.2	4.7
	Bottom	15.7	32.8	8.8
Sum of bottoms	Top	14.4	32.0	8.1
	Bottom	107.3	35.0	59.9
Total		145.9		81.5
Loss		19.7		

The losses are almost entirely due to sampling.

It indicates that more than 50% of the initial material is no longer fractioned, *viz.*, the cut with an s. p. p. of 35°.

Since small amounts of the lower fractions were lost by solubility in the alcohol–benzene mixture, it was decided to investigate this lower portion by a somewhat modified technique.

A solution containing two hundred and fifty grams of crepe rubber was prepared and therefrom fractions A_1 and A_2 were obtained as before. After discarding the remainder of the rubber, these two fractions, A_1 and A_2, were redissolved in their original solvent, thus avoiding the loss of portions which were so soluble in the alcohol–benzene mixture that they could not be completely precipitated by chilling. These combined fractions were then treated by a procedure identical to the primary fractionation, and a fraction B_1 collected and stored. The supernatant liquid was then chilled. This precipitated some more rubber; one-half of the chilled liquid was then decanted and discarded. The chilled precipitate was then redissolved by warming in the retained half of the liquid. The whole procedure was repeated to give fractions B_2, B_3, etc. The results of this special fractionation are listed in Table IV and represented on the diagram.

TABLE IV

SPECIAL FRACTIONATION

Fractions	Amounts, g.	S. p. p.	% based on a total of 233 g. as 100%
B_1	48.4	33.7	20.7
B_2	29.2	31.4	12.5
B_3	12.0	29.4	5.1
B_4	9.4	27.9	4.0
B_5	6.5	26.1	2.8

Results.—The diagram and the tables show that the present procedure separated a single component, characterized by an s. p. p. of 35.0%. The amount of this component exceeded 55% of the original rubber. A quantity of less than 20% of the original rubber was separated as a less soluble fraction, and was not investigated further; it probably still con-

tained an appreciable amount of the component s. p. p. 35°. The highly soluble part of the rubber, amounting to about 25%, was fractioned; it failed to reveal the presence of an important constituent, except more of the component s. p. p. 35°.

There was quite a difference in appearance between the high and low s. p. p. fractions. The rubber of s. p. p. 35.0° was very tough, non-tacky, and somewhat opaque. The lower fractions were soft, but white in color, showing no apparent signs of oxidation. The insoluble portion was yellow, in its fresh state, and darkened on standing. It had little elasticity and resembled horn more than rubber.

Conclusion.—It is therefore concluded that the original rubber specimen consisted of, (1) a soluble portion containing several individuals and totaling more than 20% of the specimen, (2) a single soluble component present in excess of 50% of the total, and (3) an insoluble portion amounting to less than 20% of the total.

Discussion.—The origin of the more soluble portions of rubber is obscure. Staudinger[2] suggests the possibility of forming such a portion by partial oxidation of the original molecule. Since precautions were taken to avoid oxidation during the course of the fractionation, it is suggested that the more soluble fractions were generated during the washing and sheeting of the original coagulate.

The present results bear a definite relation to two controversial points.

(1) Staudinger[2] has advanced the view that rubber is made up of a series of polymer homologs of many different lengths. It is now shown that though such a series may exist, to a limited extent, in the more soluble portions of rubber, the main constituent is one definite polymer.

(2) It is generally felt that in order to obtain a good grade of soft rubber goods, a two-phase system is required, implying that both sol and gel rubber should be present. Sol rubber, separated from gel, has been satisfactorily vulcanized, but the completeness of the separation was questioned. It is now found that pure sol rubber of s. p. p. 35° does give a satisfactorily vulcanized material (500% elongation and 4100 lb. tensile strength). That this sol rubber is of high purity is practically certain.

Experimental

Determination of the Standard Precipitation Point.—A 1.288-g. sample of the rubber (free from solvent) is placed in a 250-cc. Erlenmeyer flask. One hundred cc. of C. P. benzene is added. The flask is set away in the dark, under carbon dioxide, until complete solution is obtained. To this solution, warmed to about 50°, is added a hot mixture of 27 cc. of benzene and 56 cc. of absolute alcohol, and the whole is stirred and intermittently warmed until entirely clear. A calibrated thermometer reading tenth degrees is placed in it and it is allowed to cool. When the mixture becomes suddenly turbid, the temperature is read. This is the experimental precipitation point. It is

[2] Staudinger and Bondy, *Ann.*, [2] **488**, 153 (1931).

reproducible to ±0.1°. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250-cc. receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to ensure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified carbon dioxide through the system, the solvents are distilled with a steam-bath. The distillate is weighed, and its refractive index is measured in a Pulfrich refractometer, at 20.0°. From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1%. By means of the chart, Fig. 2, paper VII, the experimental precipitation point is then corrected to standard conditions, *viz.*, 28.55% alcohol and 0.85% rubber. This is the s. p. p. Including experimental errors and corrections, the s. p. p. determination is correct within ±0.2°.

Summary

1. Fractional precipitation has been used to determine and isolate the constituents of the rubber hydrocarbon.

2. A "standard precipitation point" has been devised and its use advanced as a physical constant of rubber.

3. The presence of a single component, amounting to more than 50% and characterized by a standard precipitation point of 35°, has been demonstrated.

4. The presence of highly soluble portions, of indeterminate s. p. p., has been shown.

COLUMBUS, OHIO

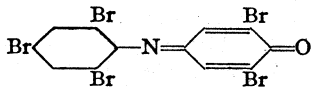
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE OXIDATION OF SYMMETRICAL TRIBROMOANILINE BY CHROMIC ANHYDRIDE IN ACID SOLUTION. II. MECHANISM[1]

BY W. H. HUNTER AND CARYL SLY

RECEIVED APRIL 11, 1932 PUBLISHED AUGUST 5, 1932

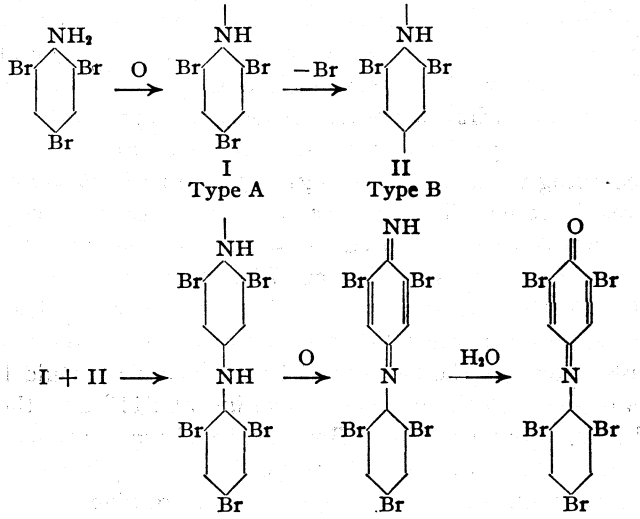
In some unpublished work performed in this Laboratory by A. G. Mayers (now deceased), it was found that symmetrical tribromoaniline, dissolved in a mixture of acetic and dilute sulfuric acids, on oxidation with chromic anhydride gave a compound with the molecular formula $C_{12}H_4ONBr$, and the structural formula



[1] Abstracted from a thesis submitted by Caryl Sly to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

Brominated N-phenylquinoneimines have been prepared by Smith and Orton[2] by first brominating *p*-hydroxydiphenylamine and then oxidizing with chromic anhydride. However, no reference could be found relative to the formation of such compounds by the oxidation of halogenated anilines.

Consideration of the probable mechanism for the formation of the above compound by oxidation of symmetrical tribromoaniline led to two widely divergent views of the reaction. Goldschmidt[3] has shown in the oxidation of anilines that a radical of the type C_6H_5NH— is first formed, which may react as such or be further oxidized to the type $C_6H_5N<$. This latter radical in his opinion was responsible for the formation of azobenzene and quinone diimine by the oxidation of aniline. The radical C_6H_5NH— is the nitrogen analog of the type A radicals which result during the oxidation of *sym.*-trihalogenated phenols.[4] Using the type A and type B radicals predicated in the case of the halogenated phenols the reaction becomes



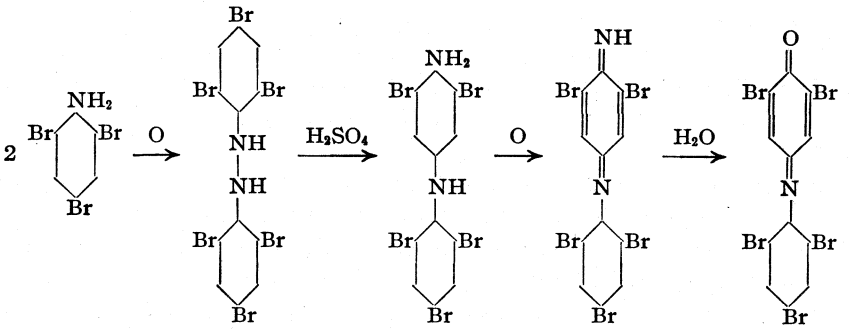
The alternative mechanism assumed the formation of *sym.*-hexabromohydrazobenzene, a *p*-semidine rearrangement of this derivative with the loss of a bromine atom, oxidation to the quinonediimine and finally hydrolysis to the quinoneimine.

In order to choose between these mechanisms an attempt was made to prepare the pentabromoquinoneimine from *sym.*-hexabromohydrazobenzene. The preparation of hexabromohydrazobenzene presented consider-

[2] Smith and Orton, *J. Chem. Soc.*, **93**, 314–326 (1908).

[3] Goldschmidt, *Ber.*, **55**, 3216 (1922).

[4] Hunter and Levine, THIS JOURNAL, **48**, 1608 (1926); Hunter and Morse, *ibid.*, **48**, 1615 (1926).



able difficulty despite the fact that it had been previously reported by Pechmann and Nold.[5]

Production of the desired hydrazo derivative from *sym.*-tribromonitrobenzene was not successful because at least one bromine was lost in alkaline reduction, a condition already observed by other workers.[6] Eventually 2,4,6,2′,4′,6′-hexabromoazobenzene was prepared by oxidizing *sym.*-tribromoaniline in pyridine solution with potassium permanganate.

In the light of our work it is extremely doubtful if Pechmann and Nold had the hexabromohydrazobenzene. Instead, it is probable they had the 2,4,2′,4′-tetrabromohydrazobenzene, since the reduction of hexabromoazobenzene according to their directions gave as the main product this tetrabromohydrazobenzene. The fact that we had the tetrabromohydrazo derivative was not at first recognized because Zincke[7] had reported the corresponding azo compound as melting at 179°, as compared with a melting point of 211° for the oxidation product of our compound. The identity of the substance, however, was established by analysis, by reduction to 2,4-dibromoaniline, and by the fact that 2,4-dibromoaniline could be oxidized with permanganate to the compound melting at 211° and then reduced back to the 2,4–dibromoaniline. Both the hexabromoazobenzene and the tetrabromoazobenzene were readily reduced to the hydrazo state by zinc dust and acetic acid, the former without loss of bromine.

All of our attempts to cause the benzidine or semidine rearrangement of the hexabromoazobenzene or hexabromohydrazobenzene met with failure. Using the azo derivative, Jacobson's method[8] or Witt's method[9] gave only reduction products. With the hydrazo derivative, concentrated hydrochloric acid or 65% sulfuric acid[10] caused only oxidation and reduction to

[5] Pechmann and Nold, *Ber.*, **31**, 564 (1898).

[6] Jackson and Bentley, *Am. Chem. J.*, **14**, 364 (1892).

[7] Zincke and Kuchenbecker, *Ann.*, **330**, 54 (1904).

[8] Jacobson, *Ann.*, **287**, 105, 110, 128 (1895).

[9] Witt, *Ber.*, **27**, 2382 (1894).

[10] Meyer, *Ber.*, **53**, 2035, 2045 (1920), reports that sulfuric acid caused rearrangement in a similar case where hydrochloric acid failed.

the azo compound and the substituted aniline. Tauber's method[11] of treating the hydrazo compound with a reducing agent and a mineral acid gave only reduction to the aniline. Similar results were obtained in the case of the tetrabromoazobenzene and tetrabromohydrazobenzene. The usual tests[12] for *o*- and *p*-semidine rearrangement products were negative.

As a final test for the formation of pentabromoquinoneimine from *sym.*-hexabromohydrazobenzene, the hydrazo compound was added to the reaction mixture which had oxidized *sym.*-tribromoaniline to the pentabromoquinoneimine. Here the only reaction was one of oxidation to hexabromoazobenzene.

In view of these results it seems probable that the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride involves the same reaction mechanism as that previously postulated for the oxidation of symmetrically halogenated phenols, with the intermediate formation of the N analogs of the type A and type B radicals.

Experimental Part

2,4,6,2',4',6'-Hexabromoazobenzene.—Twenty grams of *sym.*-tribromoaniline was dissolved in a mixture of 90 cc. of pyridine and 46 cc. of water and the solution heated to 75°. To this solution 40 g. of finely pulverized potassium permanganate was added in small portions, shaking after each addition until the permanganate color had disappeared. The copious precipitate of manganese dioxide was filtered off, washed with cold water, dried and thoroughly extracted with chloroform. The chloroform solution was evaporated to dryness, and the resulting solid suspended in 100 cc. of acetic acid held at 80°. The insoluble purple precipitate was pure hexabromoazobenzene, m. p. 212–213° (uncorr.); yield, 40%.

A 20% yield was obtained by heating 1 g. of *sym.*-tribromoaniline, 5 cc. of pyridine and 1 cc. of 17% sodium hypochlorite solution, diluting with 50 cc. of water and treating the insoluble precipitate as above.

Pechmann and Nold[5] described the compound as red needles, but in every case our product was a dull violet color, although solutions of it were red. The substance is readily soluble in hot chloroform or benzene, moderately soluble in these solvents cold and practically insoluble in either hot or cold alcohol, acetic acid, ether, and acetone.

Anal. Calcd. for $C_{12}H_4N_2Br_6$: Br, 73.17, N, 4.27. Found: Br, 73.17; N, 4.29.

2,4,2',4'-Tetrabromoazobenzene.—Using the same procedure described for the hexabromo derivative, 20 g. of 2,4-dibromoaniline dissolved in a mixture of 40 cc. of pyridine and 40 cc. of water was treated with 40 g. of potassium permanganate. The dried mixture of manganese dioxide and azo derivative was extracted with 200 cc. of benzene until no further coloration of the benzene resulted. On cooling the benzene solution a considerable portion of the azo compound crystallized as red needles. These were filtered off, the mother liquor evaporated to 50 cc. and 100 cc. of hot 95% alcohol added; yield, 40%; m. p. 211° (uncorr.).

Fifty to sixty per cent. yields were also obtained by reducing *sym.*-hexabromoazobenzene suspended in alcohol with zinc dust and ammonium chloride and then oxidizing the product thus formed in acetic acid with chromic anhydride.

[11] Tauber, *Ber.*, **25**, 1022 (1892).

[12] Witt and Schmidt, *ibid.*, **25**, 1017 (1892), and Ikuta, *Ann.*, **243**, 281 (1887); *Ber.*, **27**, 2707 (1894).

The substance crystallizes in red needles from benzene, is very soluble in either hot chloroform or benzene, slightly soluble in hot acetic acid and practically insoluble in alcohol.

Anal. Calcd. for $C_{12}H_6N_2Br_4$: Br, 64.26; N, 5.62. Found: Br, 63.74, 63.61; N, 5.63, 6.03.

2,4,2',4'-Tetrabromohydrazobenzene.—Two and one-half grams of tetrabromoazobenzene dissolved in a boiling mixture of 40 cc. of benzene and 5 cc. of acetic acid was stirred vigorously with 1 to 3 g. of zinc dust, added in small portions. The excess zinc was filtered from the colorless solution and the filtrate evaporated to 5 cc. One cc. of water and 5 cc. of acetic acid were added, and the solution chilled, giving colorless needles of m. p. 123–124° (uncorr.); yield, 80%. Reduction with stannous chloride gave 2,4-dibromoaniline.

Anal. Calcd. for $C_{12}H_8N_2Br_4$: Br, 64.00; N, 5.60. Found: Br, 63.70; N, 5.99.

N,N'-Diacetyl-2,4,2',4'-tetrabromohydrazobenzene.—One gram of tetrabromohydrazobenzene was added to 25 cc. of cold acetic anhydride and the mixture allowed to stand for two days, then heated to 40° and cooled. The azo derivative which had formed was filtered off and the excess acetic anhydride destroyed with hot water. The insoluble material after treatment with water was recrystallized from dilute alcohol as colorless crystals, m. p. 178–179°C. (uncorr.); yield, 40%.

Anal. Calcd. for $C_{16}H_{12}O_2N_2Br_4$: Br, 54.80. Found: Br, 54.22.

Rearrangement Experiments.—All of our attempts to rearrange either the hexabromohydrazobenzene or the tetrabromohydrazobenzene met with failure. Mineral acids without a reducing agent present and at elevated temperatures gave only the azo

TABLE I

REARRANGEMENT EXPERIMENTS ON HEXABROMOHYDRAZOBENZENE

Reaction of 1 g. of hexabromohydrazobenzene and	Hexabromoazobenzene, g.	*Sym.*-tribromoaniline, g.	Recovered, %
20 cc. concd. HCl, sealed tube, 130°	0.46	0.51	97
20 cc. 66% H_2SO_4, sealed tube, 150°	.43	.52	95
25 cc. abs. alcohol, 10 cc. concd. HCl, 1 g. $SnCl_4$, 80° for 12 hrs.; stood for 3 days	.40	.55[a]	95
25 cc. abs. alcohol, 10 cc. 66% H_2SO_4, 80° for 12 hrs., stood for 3 days	.42	.52[a]	94
30 cc. cold abs. alcohol, 1 g. $SnCl_2 \cdot H_2O$, 5 cc. concd. HCl, stood for 48 hrs.	.93 unchanged hydrazo	.05	98

[a] Contained small amounts of unchanged hexabromohydrazobenzene.

TABLE II

REARRANGEMENT EXPERIMENTS ON TETRABROMOHYDRAZOBENZENE

Reaction of 1 g. of tetrabromohydrazobenzene and	Tetrabromoazobenzene, g.	2,4-Dibromoaniline, g.	Recovered, %
10 cc. concd. HCl, sealed tube, 130°	0.45	0.47	92
10 cc. 66% H_2SO_4, sealed tube, 100–130°	.45	.42	87
25 cc. abs. alcohol, 10 cc. concd. HCl, 1 g. $SnCl_4$, 80° for 12 hours, stood for 3 days	.48	.40	88
25 cc. abs. alcohol, 10 cc. 66% H_2SO_4, 80° for 12 hrs., stood for 3 days	.47	.46	93
25 cc. abs. alcohol, 1 g. $SnCl_2 \cdot 2H_2O$, 5 cc. concd. HCl, stood for 48 hrs.	.85 unchanged hydrazo	.12	97

derivative and the aniline, while in the cold, stannous chloride in the presence of hydrochloric acid gave the aniline along with the unchanged hydrazobenzene.

The tables indicate the conditions of attempted rearrangement and the products isolated.

Summary

1. A study of the properties of *sym.*-hexabromohydrazobenzene has shown that it cannot be responsible for the formation of a pentabromoquinoneimine obtained by the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride. It is, therefore, probable that N analogs of the type A and type B radicals postulated in the oxidation of *sym.*-halogenated phenols play the important role.

2. *Sym.*-hexabromohydrazobenzene and 2,4,2′,4′-tetrabromohydrazobenzene do not undergo the benzidine type of rearrangement. Instead they oxidize and reduce to the corresponding azo and aniline derivatives in the presence of a mineral acid without a reducing agent; in the presence of a reducing agent they are split to the anilines.

3. A method for the preparation of azo compounds is described.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

THE INTERACTION OF PHENYLARSINES WITH PHENYLHALOARSINES[1]

BY F. F. BLICKE AND L. D. POWERS

RECEIVED APRIL 13, 1932 PUBLISHED AUGUST 5, 1932

Several years ago it was announced by Steinkopf and Smie[2] that phenyldichloroarsine and diphenylarsine react to form triphenylchlorodiarsyl.

$$C_6H_5AsCl_2 + (C_6H_5)_2AsH = C_6H_5(Cl)As—As(C_6H_5)_2 + HCl$$

Since we wished to prepare triphenylhydroxydiarsyl,[2a] hydrolysis of the corresponding chloro compound suggested itself as a preparative procedure. Phenyldichloroarsine and diphenylarsine were allowed to react in the proportions used by the above-mentioned investigators but instead of triphenylchlorodiarsyl, arsenobenzene and diphenylchloroarsine were obtained in yields which correspond closely to those calculated from equation A.[3]

[1] This paper represents one part of a dissertation submitted to the Graduate School by L. D. Powers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Steinkopf and Smie, *Ber.*, **59**, 1459 (1926).

[2a] It is of interest to note that Wieland and co-workers [*Ber.*, **44**, 898 (1911); *ibid.*, **48**, 1118 (1915)] were unable to obtain the corresponding nitrogen analog R_2N–NR(OH).

[3] The very unsharp melting point (164–179°) of the "triphenylchlorodiarsyl" obtained by Steinkopf and Smie indicates that these investigators really had a mixture of compounds. The identity of the material obtained by them was based on the result

A $4C_6H_5AsCl_2 + 4(C_6H_5)_2AsH = 2C_6H_5As{=}AsC_6H_5 + 4(C_6H_5)_2AsCl + 4HCl$

The reaction between diphenylarsine, as well as phenylarsine, and each of the following compounds was then investigated: phenyldichloroarsine, phenyldi-iodoarsine, diphenylchloroarsine and diphenyliodoarsine.

It has been shown in separate experiments that two molecular equivalents of phenyldichloroarsine and four equivalents of diphenylarsine yield arsenobenzene and tetraphenyldiarsyl (B), that equivalent amounts

B $2C_6H_5AsCl_2 + 4(C_6H_5)_2AsH = C_6H_5As{=}AsC_6H_5 + 2(C_6H_5)_2As{-}As(C_6H_5)_2 + 4HCl$

C $2C_6H_5AsCl_2 + 2(C_6H_5)_2As{-}As(C_6H_5)_2 = 4(C_6H_5)_2AsCl + C_6H_5As{=}AsC_6H_5$

A $4C_6H_5AsCl_2 + 4(C_6H_5)_2AsH = 2C_6H_5As{=}AsC_6H_5 + 4(C_6H_5)_2AsCl + 4HCl$

of phenyldichloroarsine and tetraphenyldiarsyl react to form diphenylchloroarsine and arsenobenzene (C) and that no reaction takes place at ordinary temperature between diphenylchloroarsine and arsenobenzene or between diphenylarsine and arsenobenzene.

When phenyldi-iodoarsine is allowed to react with diphenylarsine in the ratio shown in formulation F diphenyldi-iododiarsyl and diphenyliodoarsine are formed. The di-iododiarsyl is produced in this instance

D $2C_6H_5AsI_2 + 2(C_6H_5)_2AsH = C_6H_5(I)As{-}As(I)C_6H_5 + (C_6H_5)_2As{-}As(C_6H_5)_2 + 2HI$

E $2C_6H_5AsI_2 + (C_6H_5)_2As{-}As(C_6H_5)_2 = C_6H_5(I)As{-}As(I)C_6H_5 + 2(C_6H_5)_2AsI$

F $4C_6H_5AsI_2 + 2(C_6H_5)_2AsH = 2C_6H_5(I)As{-}As(I)C_6H_5 + 2(C_6H_5)_2AsI + 2HI$

due to the fact that phenyldi-iodoarsine, unlike phenyldichloroarsine, reacts at ordinary temperature with arsenobenzene.[4] The mechanism of this reaction may, possibly, be explained on the basis of reactions D and E since these reactions have been established by separate experiments.

Steinkopf and Smie[5] mixed phenyldi-iodoarsine and diphenylarsine in the ratio expressed in formulation D and stated that phenyliodoarsine, $C_6H_5As(I)H$, and diphenyliodoarsine were produced. The "phenyliodoarsine" described by them was, undoubtedly, diphenyldi-iododiarsyl. Furthermore, these investigators stated[6] that one molecular equivalent of phenyldi-iodoarsine and two equivalents of diphenylarsine react to form pentaphenyltriarsine, $(C_6H_5)_2As{-}As(C_6H_5){-}As(C_6H_5)_2$; neither melting point nor any other property of this compound was recorded. The nature of the reaction product was merely deduced from the fact that treatment of the reaction product with iodine yielded phenyldi-iodoarsine and diphenyliodoarsine in a certain ratio. The experimental data yield

of a chlorine analysis and on the fact that phenylarsonic acid and diphenylarsinic acid were obtained upon oxidation of the reaction product. Obviously, the same data would be obtained from a mixture which consisted of arsenobenzene and twice the molecular quantity of diphenylchloroarsine.

[4] Blicke and Smith, THIS JOURNAL, **52**, 2942 (1930).

[5] Ref. 2, p. 1460.

[6] Ref. 2, p. 1461.

little or no evidence in favor of the contention that pentaphenyltriarsine was formed in this reaction.

Diphenylchloroarsine and diphenylarsine, dissolved in ether, yielded tetraphenyldiarsyl and the interaction of these substances represents a satisfactory method for the preparation of the diarsyl.

G $(C_6H_5)_2AsCl + (C_6H_5)_2AsH = (C_6H_5)_2As—As(C_6H_5)_2 + HCl$

Diphenyliodoarsine and diphenylarsine, dissolved in alcohol, also react to form tetraphenyldiarsyl.

Phenyldichloroarsine reacts with phenylarsine to form arsenobenzene.

H $C_6H_5AsCl_2 + C_6H_5AsH_2 = C_6H_5As{=}AsC_6H_5 + 2HCl$

Phenyldi-iodoarsine and phenylarsine yield the same reaction product when they are mixed in equivalent amounts. However, if three molecular equivalents of the di-iodo compound react with one equivalent of phenylarsine diphenyldi-iododiarsyl is formed.

I $3C_6H_5AsI_2 + C_6H_5AsH_2 = 2C_6H_5(I)As—As(I)C_6H_5 + 2HI$

When diphenylchloroarsine and phenylarsine are allowed to react in the ratio expressed in the following equation arsenobenzene and tetra-

J $4(C_6H_5)_2AsCl + 2C_6H_5AsH_2 = C_6H_5As{=}AsC_6H_5 + 2(C_6H_5)_2As—As(C_6H_5)_2 + 4HCl$

phenyldiarsyl are produced. If the above-mentioned compounds are mixed in equimolecular quantities arsenobenzene and tetraphenyldiarsyl are again formed as reaction products. Steinkopf and Smie[7] stated that diphenylchloroarsine and phenylarsine react to form triphenyldiarsyl, $(C_6H_5)_2As—As(H)C_6H_5$. These investigators merely analyzed their reaction product, which was not characterized by a melting point, and considered the arsenic analysis and the fact that a mixture of phenylarsonic and diphenylarsinic acids was obtained upon oxidation of their product with nitric acid sufficient proof for the claim that triphenyldiarsyl had been formed. The data published by Steinkopf and Smie would be almost identical with that obtained from a mixture which consisted of one equivalent of arsenobenzene and two equivalents of tetraphenyldiarsyl.

Diphenyliodoarsine and phenylarsine, mixed in the proportion given below, yield arsenobenzene and tetraphenyldiarsyl.

K $4(C_6H_5)_2AsI + 2C_6H_5AsH_2 = C_6H_5As{=}As3_6H_5 + 2(C_6H_5)_2As—As(C_6H_5)_2 + 4HI$

Experimental Part

Since phenylarsine, diphenylarsine and many of the reaction products absorb oxygen with great rapidity, it was necessary to carry out all experiments in an inert atmosphere. The apparatus used for this purpose is shown in the accompanying sketch. By manipulation of the stopcocks the free radical bulb, as well as the buret above it, was evacuated and filled with dry, oxygen-free nitrogen. This operation was repeated several times until all air had been removed from the system. The arsine was introduced

[7] Ref. 2, p. 1458.

into the buret from the reservoir[8] and allowed to flow into the evacuated radical bulb. The walls of the buret were then washed free from arsine by the introduction of ether, benzene or alcohol from the dropping funnel. After the radical bulb had been filled with nitrogen, it was disconnected and the substance added with which the arsine was to react.[9] In the event that pressure developed in the bulb the side arm of the latter was connected to the mercury trap shown in the lower left-hand corner of the diagram or photograph.

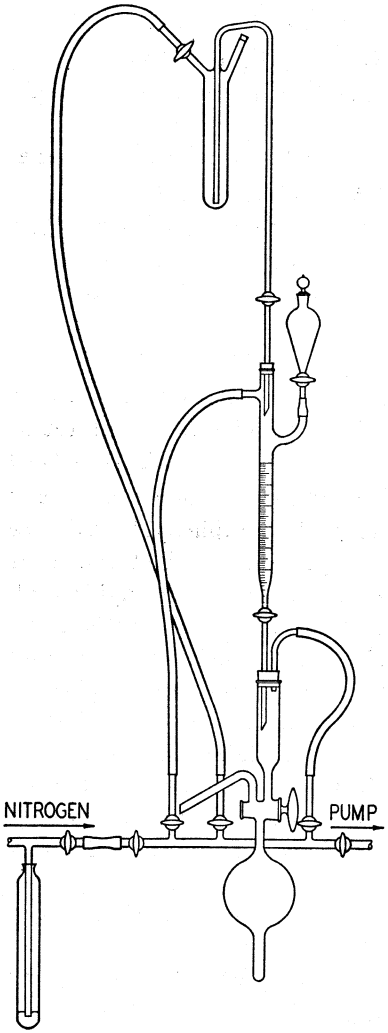


Fig. 1.

All solvents were saturated with nitrogen prior to use and only the absolute grades of alcohol and ether were employed. A dextrin–mannitol–glycerol stopcock lubricant[10] was found to be very satisfactory when ether or benzene was used as a solvent. The melting points of compounds which absorb oxygen were determined in a sealed tube filled with nitrogen. The reaction mixtures were shaken for at least twenty-four hours. Absorption experiments were carried out in bromobenzene solution.

Phenyldichloroarsine and Diphenylarsine (A, B).—Six and ninety-two hundredths grams (5.32 cc., 0.030 mole) of diphenylarsine[11] was added to 8.50 g. (0.038 mole) of phenyldichloroarsine, dissolved in 50 cc. of ether. After a short time a heavy, crystalline precipitate had formed. The ether was decanted into a second radical bulb and the precipitate, which proved to be arsenobenzene, washed with ether a number of times until it was entirely free from halogen compounds;[12] mixed m. p. 210–212°. The material was recrystallized from xylene for analysis.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.23, 49.38.

The yield was 3.96 g. or 87% of the calcd. amount.

[8] After each arsine had been prepared it was distilled directly into a reservoir of the type shown through the short side arm. In such containers the arsines can be protected from oxidation for a long time.

[9] In some instances the arsine was introduced after the other component of the reaction had been placed in the radical bulb.

[10] The directions for the preparation of this lubricant were furnished us by C. C. Meloche and W. G. Fredrick.

[11] The following constants were determined for diphenylarsine: d_{25}^{25} 1.30; b. p. 158–160° under 16 mm. pressure.

[12] Arsenobenzene absorbs oxygen rapidly unless it is washed free from all traces of halogen compounds.

The ether layer from the reaction mixture, which contained diphenylchloroarsine and unchanged phenyldichloroarsine, was treated with alkali in order to convert the chlorides into oxides. Phenylarsine oxide dissolved in the aqueous layer while 6.78 g. or 95% of the calcd. amount of tetraphenylarsyl oxide was isolated from the ether layer. The latter oxide, after it had been washed with petroleum ether (30–60°), melted at 94–95°.

Mixed in the ratio shown in formulation B, 4.6 g. (3.5 cc., 0.02 mole) of diphenylarsine reacted with 2.2 g. (0.01 mole) of phenyldichloroarsine, dissolved in 25 cc. of ether, to form a bulky, crystalline precipitate. In order to expel the hydrogen chloride formed[13] the ether was removed by distillation, the residue treated with 25 cc. of ether and the solvent again expelled. After the product had been dried for two hours under 15 mm. pressure the mixture was extracted a number of times with ether in order to remove tetraphenyldiarsyl; about 500 cc. of ether was used for this purpose. The tetraphenyldiarsyl obtained melted at 125–129°;[14] 0.887 g. of the material absorbed 43 cc. (N. T. P.) of oxygen, which is the calculated amount. The arsenobenzene, which remained as a residue, weighed 1.3 g.; calcd. amount 1.5 g.; mixed m. p. 209–211°.

Phenyldichloroarsine and Tetraphenyldiarsyl (C).—Two and forty-five hundredths grams (0.005 mole) of tetraphenyldiarsyl was allowed to react with 1.2 g. (0.005 mole) of phenyldichloroarsine, dissolved in 100 cc. of ether. About three-fourths of the solvent was then removed by distillation and after some time a precipitate of arsenobenzene was obtained. The supernatant liquid was decanted and the arsenobenzene washed free from chlorine compounds with ether. There was isolated 0.22 g. of the arseno compound which melted at 196–206°. The ether washings were exposed to air and the residue obtained after evaporation of the solvent was treated with a mixture of ether and low-boiling petroleum ether; 0.92 g. of diphenylchloroarsine, m. p. 41–42°, was obtained.

Phenyldi-iodoarsine and Diphenylarsine (D, F).—Diphenyldi-iododiarsyl precipitated almost immediately when 4.06 g. (0.01 mole) of phenyldi-iodoarsine, dissolved in 100 cc. of ether, was mixed with 2.30 g. (0.01 mole) of diphenylarsine. After twenty-four hours the solvent was completely removed by distillation and the residue, a mixture of diphenyldi-iododiarsyl and tetraphenyldiarsyl, dried for two hours under diminished pressure in order to expel hydrogen iodide. The mixture was extracted four times with 50-cc. portions of ether and the ether layers, which contained tetraphenyldiarsyl, decanted into a second radical bulb. The residue of diphenyldi-iododiarsyl weighed 2.43 g.; calcd. amount 2.79 g.; m. p. 176–179°.[15]

The combined ether extracts were shaken with alkali to remove traces of iodine compounds and the solvent then removed. An oil was obtained which was treated with 25 cc. of alcohol; after the solvent had been partially removed by distillation tetraphenyldiarsyl separated in crystalline form. After recrystallization from absolute alcohol, 1.3 g. of material was obtained which melted at 128–130°.

Anal. Calcd. for $C_{24}H_{20}As_2$: As, 32.73. Found: As, 32.58, 32.28.

From the alcoholic mother liquor 0.4 g. more of the diarsyl was obtained. The calcd. yield is 2.29 g. Upon exposure to oxygen, 0.587 g. of the compound absorbed 30 cc. (N. T. P.) of the gas; calcd. amount 29 cc.

In accordance with formulation F 2.30 g. (0.01 mole) of diphenylarsine was added to 8.11 g. (0.02 mole) of phenyldi-iodoarsine, dissolved in 50 cc. of ether. A copious

[13] Removal of the hydrogen chloride seems to facilitate the quantitative isolation of arsenobenzene and also prevents oxidation of the latter.

[14] Blicke and Smith, THIS JOURNAL, **51**, 2275 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 782 (1930).

[15] Blicke and Smith, THIS JOURNAL, **52**, 2943 (1930).

yellow precipitate of diphenyldi-iododiarsyl formed immediately. The ether layer was decanted, the precipitate washed a number of times with ether and then dried at 50° under 15 mm. pressure for two hours. The product melted at 177–178°; yield 5.32 g.; calcd. yield 5.57 g. From the ether mother liquor an oil was obtained which solidified in the form of a yellow crystalline mass when cooled; m. p. 39–41°. This material, diphenyliodoarsine, weighed 3.76 g. in the crude state; calcd. yield 3.55 g.

Phenyldi-iodoarsine and Tetraphenyldiarsyl (E).—Four and one-tenth grams of phenyldi-iodoarsine was added to about 2 g. of tetraphenyldiarsyl, dissolved in benzene. Diphenyldi-iododiarsyl soon precipitated from the mixture; after it had been washed with ether it melted at 175–177° and weighed 1.4 g. The benzene mother liquor and ether washings were combined and shaken with alkali in order to convert the halides to oxides. The diphenyliodoarsine was isolated, therefore, as tetraphenylarsyl oxide; yield 1.4 g. Eight-tenths of a gram of phenylarsine oxide was also obtained as the result of hydrolysis of the excess phenyldi-iodoarsine used.

Diphenylchloroarsine and Diphenylarsine (G).—To 3.4 g. (0.015 mole) of diphenylarsine there was added 4.4 g. (0.016 mole) of diphenylchloroarsine, dissolved in 50 cc. of ether. After two hours the solution was concentrated to a volume of about 10 cc., whereupon tetraphenyldiarsyl precipitated. The ether mother liquor was decanted, a small quantity of fresh ether added and the ether suspension shaken a number of times with water until all hydrochloric acid had been removed. The ether was then removed by distillation and the material dried under diminished pressure; m. p. 124–127°. The yield was 6.0 g.; calcd. yield, 6.8 g.

Diphenyliodoarsine and Diphenylarsine.—Tetraphenyldiarsyl precipitated instantly when 3.56 g. of diphenyliodoarsine, dissolved in 50 cc. of alcohol, was added to 2.30 g. of diphenylarsine. The diarsyl was purified in the manner described above; m. p. 129–130°. The yield was 3.4 g.; calcd. amount, 4.6 g.

Phenyldichloroarsine and Phenylarsine (H).—A mixture prepared from 3.34 g. (0.015 mole) of phenyldichloroarsine, 2.30 g. (0.015 mole) of phenylarsine and 65 cc. of ether was shaken for twenty-four hours. The ether layer was decanted from the crystalline material into a second radical bulb and the solid product washed with ether until it was completely free from hydrogen chloride. The material, which was arsenobenzene, weighed 1.94 g.; m. p. 209–211°. From the ether layer 2.20 g. more of arsenobenzene was obtained. The total yield was 4.14 g.; calcd. amount, 4.56 g.

Phenyldi-iodoarsine and Phenylarsine (I).—No apparent reaction took place after 2.30 g. (0.015 mole) of phenylarsine had been shaken with 1.68 g. (0.01 mole) of phenylarsine oxide, dissolved in benzene, for twenty-four hours.[16] There was then added 12.2 g. (0.03 mole) of phenyldi-iodoarsine, dissolved in benzene. Diphenyldi-iododiarsyl precipitated immediately; m. p. 178–180°. The yield was 14.3 g.; calcd. yield, based on 0.04 mole of phenyldi-iodoarsine, 14.8 g.

Diphenylchloroarsine and Phenylarsine (J).—When 12 g. (0.045 mole) of diphenylchloroarsine was added to 2.97 g. (0.019 mole) of phenylarsine, dissolved in 100 cc. of ether, there was no visible sign of reaction. Twenty-five cubic centimeters of alcohol was then added, whereupon a crystalline precipitate soon began to form. After twelve hours the solvents were removed by distillation and the residue dried for two hours under 15 mm. pressure in order to remove hydrogen chloride completely. One hundred cubic centimeters of ether was added to the residue, the mixture shaken for several hours and the ether solution of tetraphenyldiarsyl decanted into a second radical bulb. This

[16] These compounds were mixed in order to determine whether or not they reacted under the given experimental conditions. The hydrogen iodide, formed subsequently as a result of the interaction of phenylarsine and phenyldi-iodoarsine, converted the phenylarsine oxide into phenyldi-iodoarsine.

process was repeated until a test portion of the ether extract left no residue upon evaporation of the solvent; about 500 cc. of ether was required. From the ether solutions there was obtained 9.08 g. of tetraphenyldiarsyl; m. p. 123–127°; calcd. yield 9.16 g. When 0.915 g. of the compound was exposed to oxygen, 47 cc. of the gas was absorbed; calcd. absorption, 45 cc. The residue after extraction of the reaction mixture with ether was pure arsenobenzene; m. p. 210–211°. The yield was 2.70 g.; calcd. yield, 3.04 g.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.57, 49.23.

In the following experiment the compounds were allowed to react in amounts which are practically equimolecular. To 5.29 g. (0.020 mole) of diphenylchloroarsine, dissolved in 100 cc. of alcohol, there was added 3.24 g. (0.021 mole) of phenylarsine; an oil precipitated which soon became crystalline. The alcohol layer was decanted into a second bulb and after complete removal of hydrogen chloride and unchanged arsine the tetraphenyldiarsyl was extracted with ether; m. p. 123–130°. The yield was 2.33 g.; calcd. yield, 4.58 g. One and fifty-four hundredths grams of arsenobenzene, m. p. 207–210°, was left as a residue; calcd. amount, 1.52 g.

The alcoholic solution which had been decanted contained the remainder of the diarsyl; the latter was allowed to oxidize in air. The alcohol was removed, the mixture of diphenylarsinic acid and tetraphenylarsyl oxide treated with sulfur dioxide and hydriodic acid in the presence of hydrochloric acid and the diphenylhaloarsines hydrolyzed to tetraphenylarsyl oxide; yield, 1.93 g.; m. p. 92–95°.

Any pentaphenyltriarsine or triphenyldiarsyl which might have been formed in this reaction would have been present in the decanted alcoholic solution and upon oxidation would have been converted into tetraphenylarsyl oxide and phenylarsine oxide; only a trace of the latter was found to be present in the oxidized solution.

Diphenyliodoarsine and Phenylarsine (K).—No apparent reaction took place when 8.50 g. (0.024 mole)[17] of diphenyliodoarsine was mixed with 1.08 g. (0.007 mole) of phenylarsine in 100 cc. of ether. Upon the addition of 25 cc. of alcohol a precipitate soon formed. After forty-eight hours the supernatant liquid was decanted into a second bulb and the precipitated arsenobenzene washed six times with 50-cc. portions of ether; m. p. 200–204°. The yield was 0.93 g.; calcd. yield, 1.07 g.

The ether–alcohol layer which had been decanted contained tetraphenyldiaryl and the excess diphenyliodoarsine. The solution was concentrated to about 15 cc., whereupon tetraphenyldiarsyl and some diphenyliodoarsine precipitated. The mother liquor was decanted and the product washed a number of times with petroleum ether (30–60°) in order to remove the iodoarsine. The yield of tetraphenyldiarsyl was 1.40 g.; m. p. 129–130°; calcd. amount, 3.21 g.

Each of the following compounds, dissolved in ether, was shaken with arsenobenzene for three days at ordinary temperature: phenyldichloroarsine, diphenylchloroarsine, diphenyliodoarsine, diphenylarsine and phenylarsine. In the case of each mixture at least 90% of each component was recovered unchanged. Furthermore, it was found that neither phenylarsine nor diphenylarsine reacts with tetraphenyldiarsyl at ordinary temperature.

Summary

The interaction of phenylarsine, as well as diphenylarsine, and each of the following compounds has been investigated: phenyldichloroarsine, phenyldi-iodoarsine, diphenylchloroarsine and diphenyliodoarsine. Substances such as tetraphenyldiarsyl, diphenyldi-iododiarsyl and arsenobenzene have been obtained as reaction products.

[17] This quantity represents an excess over that demanded by the formulation.

It seems that compounds such as phenyliodoarsine, triphenyldiarsyl, triphenylchlorodiarsyl and pentaphenyltriarsine are not produced by interaction of the above-mentioned arsines although the formation of these substances has been reported by other investigators.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON NITROGENOUS GLYCOSIDES. I. THE UTILIZATION OF GLYCOSE ISOCYANATES FOR GLYCOSIDE SYNTHESES

BY TREAT B. JOHNSON AND WERNER BERGMANN[1]

RECEIVED APRIL 14, 1932 PUBLISHED AUGUST 5, 1932

So far as the writers are aware, only one sugar isocyanate derivative has been described in the chemical literature, namely, tetraacetyl-*d*-glycose-*l*-isocyanate, $C_{14}H_{19}O_9NCO$. This interesting compound was described by Emil Fischer in a paper entitled "Synthese neuer Glycoside," in 1914[2] but since this publication, apparently no attention has been paid to its chemistry. Fischer obtained this sugar derivative by the action of silver cyanate on tetraacetobromoglycose, but the chief product of this reaction was an amorphous substance having the same composition as the glycose isocyanate but whose constitution was not established by Fischer.[3]

We have now repeated Fischer's preliminary experiments in order to obtain his isocyanate derivative for new glycoside syntheses. We find that silver cyanate interacts with tetraacetylbromoglycose in xylene solution to give, besides resinous substances, three definite compounds which have been identified, namely, two modifications of the glycose isocyanate (A and B), melting at 120 and 92°, respectively, and the amorphous substance previously described by Fischer as a product of this reaction. We conclude that this amorphous material is without doubt impure *sym.*-octaacetyl-*d*-diglycose urea, which is formed by the interaction of tetraacetylglycose isocyanate with water. It can be purified easily to give a beautiful crystalline substance melting at 160–161°. That this is octaacetyl-glycose urea is not only established by the results of our analyses, but also by its characteristic behavior toward aqueous ammonia. By treatment with this reagent it is transformed by hydrolysis smoothly into *sym.*-*d*-diglycose urea. The

[1] Sterling Research Assistant in Organic Chemistry, 1931–1932.

[2] E. Fischer, *Ber.*, **47**, 1377 (1914).

[3] Fischer also examined the behavior of silver isothiocyanate toward tetraacetylbromoglycose and observed the smooth formation of the corresponding glycose-isothiocyanate derivative, $C_{14}H_{19}O_9NCS$. Here also practically no attention has been paid to the chemistry of this mustard oil since Fischer's work in 1914. The results of a new research dealing with specific reactions of this interesting compound will be discussed in a future paper from this Laboratory by Miss Katherine Haring.

latter glycoside proved to be identical with the diglycose urea prepared recently by Helferich and Kosche[4] by the action of aqueous ammonia on octabenzoyldiglycose urea.

Tetraacetyl-*d*-glycose-*l*-isocyanate is characterized by its behavior toward ammonia and alcohol. By the action of aqueous ammonia it is converted smoothly into the glycose urea previously described by Schoorl.[5] The lower melting modification of the glycose isocyanate is unstable and rearranges on heating into Fischer's original glycose isocyanate, melting at 120°. The behavior toward alcohol is also characteristic of the isocyanate structure. We observed that *n*-amyl alcohol and ethylene chlorohydrin both interact smoothly at the boiling point of the respective alcohols, giving the corresponding urethans. A complete description of these various compounds and their preparation is given in the experimental part of this paper.

Tetraacetyl-*d*-glycose-*l*-isocyanate promises to be a fruitful starting point for the development of several new and important syntheses of biochemical interest. Our future program calls for coupling with various amino acids and peptide combinations leading to the formation of important glycosidoureide constructions.[6]

Experimental Part

Tetraacetyl-*d*-glycose-*l*-isocyanate, $C_{14}H_{19}O_9NCO$ (A).—To a solution of 33 g. of tetraacetobromoglycose in 120 cc. of xylene, dried over sodium, 12 g. of freshly prepared, dried and pulverized silver cyanate is added. The reaction flask is connected with a rubber stopper fitted with a calcium chloride tube and heated on the steam-bath with frequent shaking. The silver cyanate soon turns yellow due to the formation of silver bromide. After one-half and one hour, respectively, 6 g. of silver cyanate is added and the mixture is finally heated for one hour more. The liquid is then filtered by suction and the insoluble silver salts are once more extracted with 80 cc. of xylene. The united liquids are then poured into 200 cc. of petroleum ether (30–60°), whereby a slightly yellow resin is precipitated. The mother liquor is at once decanted from the resin, mixed with 100 cc. more petroleum ether and allowed to stand overnight. One thus obtains a crystalline product, which consists of two distinctly different forms of crystals, needles and blocks. The yield of crystalline material is about 16–17 g. The melting point fluctuates between 80 and 110°, according to the proportion of needles or blocks which is obtained. The crystalline material is filtered and washed with petroleum ether.

This reaction product is extracted several times with anhydrous ether, when the needle form dissolves. The fraction insoluble in ether is dissolved in anhydrous chloroform, and ether then finally added until a separation of crystals begins. Under these conditions the beautiful crystalline glycose isocyanate "A" is obtained which melts sharply at 120°.

Anal. Calcd. for $C_{15}H_{19}O_{10}N$: C, 48.24; H, 5.13; N, 3.75. Found: C, 48.37;

[4] Helferich and Kosche, *Ber.*, **59**, 69 (1926).

[5] Schoorl, *Rec. trav. chim.*, **22**, 63 (1903).

[6] We have observed also that silver cyanide and tetraacetylbromoglycose interact to give a beautiful crystalline isonitrile. The study of this substance will receive our attention later.

H, 5.19; N, 3.72. *Optical Rotation.* 0.8345 g. subs. in 25 cc. of $CHCl_3$; l = 2 dm.; $\alpha = -0.55°$; $[\alpha]_D^{18}$ $-8.3°$.

These analytical results, and the fact that the product is readily dissolved in concentrated ammonia giving *d*-glycose-urea, are conclusive evidence that the compound is the tetraacetyl-*d*-glycose-*l*-isocyanate previously described by E. Fischer.[2]

Tetraacetyl-*d*-glycose-*l*-isocyanate, $C_{14}H_{19}O_9NCO$ **(B).**—The ether solution of the above-mentioned needles is diluted with petroleum ether until cloudy. After some time, needles separate which are filtered off, dissolved in anhydrous ether and reprecipitated with petroleum ether. After repeating this precipitation again, well-developed needle-like crystals were obtained melting at 92°.

Anal. Calcd. for $C_{15}H_{19}O_{10}N$: C, 48.24; H, 5.13; N, 3.75. Found: C, 48.26; H, 5.24; N, 3.84.

In all its reactions this glycose isocyanate modification "B" behaves like Fischer's compound "A." It rearranges into Fischer's isocyanate "A" if it is heated at its melting point. After cooling the fused mass and then reheating in a capillary tube, it melted at 115–120°. If a solution of the glycose isocyanate "B" in ether is mixed with petroleum ether, at first needles of this isocyanate will separate, but these slowly undergo a transformation, on standing, into the characteristic blocks of the isocyanate "A." During each recrystallization of the isocyanate "B" some of the isomeric modification "A" is always formed, which leads the authors to the conclusion that the modification "B" has not yet been obtained entirely pure and free from Fischer's glycose isocyanate.

Experience has shown that the highest yield of the isomer "B" is obtained if one filters the original xylene solution from the silver salts directly into a large excess of petroleum ether. At first a colorless amorphous mass separates, which soon takes on a crystalline form. This usually melts between 80–90° and probably consists of about 80% of the lower melting isomer.

Sym.-Octaacetyl-*d*-diglycose Urea, $(C_{14}H_{19}O_9)NHCONH$ $(C_{14}H_{19}O_9)$.—The amorphous precipitate first obtained during the preparation of the tetraacetylglycose isocyanate is dissolved in xylene and carefully reprecipitated with petroleum ether, when it deposits again in the amorphous form. This product is then dissolved in ethyl acetate and reprecipitated several times by addition of ether and finally recrystallized from hot alcohol. On cooling this alcohol solution, needles were finally obtained which melted at 164°. This octaacetyl-diglycose urea is easily soluble in ethyl acetate, benzene, warm alcohol, acetone, difficultly soluble in hot water and insoluble in ether and petroleum ether. Large quantities of this urea may also be obtained easily by digesting the crude tetraacetyl-*d*-glycose-*l*-isocyanate in aqueous acetone and then precipitating the urea with water.

Anal. Calcd. for $C_{29}H_{40}O_{19}N_2$: C, 48.04; H, 5.56. Found: C, 48.04; H, 5.72. *Optical Rotation.* 0.0615 g. subs. in 3.2 cc. of $CHCl_3$; l = 1 dm.; $\alpha = -0.07°$; $[\alpha]_D^{26}$ $-3.7°$.

Preparation of Sym.-*d*-diglycose Urea, $(C_6H_{11}O_5)NHCONH(C_6H_{11}O_5)$.—The octaacetyl-*d*-diglycose urea is suspended in ten times its weight of concentrated aqueous ammonia and the solution allowed to stand for three days. The urea finally dissolves completely. The solution is then concentrated in a vacuum, leaving behind an oily residue which easily dissolves in water. On adding alcohol to this aqueous solution the diglycose urea separates in a crystalline condition. It is purified by crystallization from dilute alcohol. When heated in a capillary tube this urea begins to turn brown at about 205°, and decomposes when heated above 230°.

Anal. Calcd. for $C_{13}H_{24}O_{11}N_2$: C, 40.61; H, 6.30. Found: C, 40.46; H, 6.16. *Optical Rotation.* 0.06633 g. subs. in 3.12 cc. of H_2O; l = 1 dm.; $\alpha = 0.73°$; $[\alpha]_D^{26}$ $-25.4°$.

This urea agrees in all its properties with the *d*-diglycose urea already described by Helferich.[4]

Tetraacetyl-*d*-glycose-*n*-amyl Urethan, $(C_{14}H_{19}O_9)NHCOOC_5H_{11}$.—Tetraacetyl-*d*-glycose-*l*-isocyanate is dissolved in 20 cc. of *n*-amyl alcohol and the solution heated to boiling for thirty minutes. After concentration *in vacuo*, an oil is obtained which dissolves in ether completely with the exception of a small amount of octaacetyl-*d*-diglycose urea present as an impurity. Dilution of this ether solution with petroleum ether (30–60°) precipitates an oil which soon crystallizes when chilled to a low temperature. By repeated recrystallizations from a mixture of ether and petroleum ether or from dilute alcohol, the amyl urethan is obtained in the form of well-developed prismatic crystals melting at 88°. This urethan is easily soluble in ethyl acetate, alcohol, chloroform, and ether, and is insoluble in petroleum ether and water.

Anal. Calcd. for $C_{20}H_{31}O_{11}N$: C, 52.04; H, 6.77; N, 3.03. Found: C, 51.90; H, 6.70; N, 2.95. *Optical Rotation.* 0.0775 g. subs. in 3.2 cc. of ether; l = 1 dm.; $\alpha = -0.16$; $[\alpha]_D^{26}$ −6.61°.

Tetraacetyl-*d*-glycose-chlorethyl Urethan, $(C_{14}H_{19}O_9)NHCOOCH_2CH_2Cl$.—Tetraacetyl-diglycose-*l*-isocyanate and an excess of ethylene chlorohydrin are heated to boiling for ten minutes, and the solution concentrated *in vacuo*. An oil was obtained which dissolved immediately in cold ether. Dilution of this ether solution with petroleum ether led to the separation of needles which melted after repeated crystallizations at 110°. Recrystallization of this substance from dilute alcohol gave a product melting very sharply at 82–83° and containing solvent of crystallization. After drying *in vacuo* at 80° the melting point was raised to 114°.

Anal. Calcd. for $C_{17}H_{24}O_{11}NCl$: C, 44.98; H, 5.33; Cl, 7.81. Found: C, 45.05; H, 5.36; Cl, 8.01. *Optical Rotation.* 0.0551 g. subs. in 3.2 cc. of ether; l = 1 dm.; $\alpha = -0.20°$; $[\alpha]_D^{26}$ −11.6°.

Summary

1. Tetraacetylbromoglycose interacts with silver cyanate in xylene solution to give three products, namely, two isomeric modifications of tetraacetyl-*d*-glycose-*l*-isocyanate melting at 92 and 120° and octaacetyl-*d*-diglycose urea.

2. The lower melting modification of the glycose isocyanate melting at 92° is rearranged by heating into the higher melting isomer (120°).

3. Tetraacetyl-*d*-glycose-*l*-isocyanate reacts with ammonia to form *d*-glycose urea and with *n*-amyl alcohol and ethylene chlorohydrin to form the corresponding urethans.

NEW HAVEN CONNECTICUT

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

REDUCTION OF ALIPHATIC SULFONIC ACID SALTS WITH PHOSPHORUS PENTABROMIDE AND PHOSPHORUS TRIBROMIDE[1]

BY W. H. HUNTER AND B. E. SORENSON

RECEIVED APRIL 18, 1932 PUBLISHED AUGUST 5, 1932

In an attempt to prepare tribromobenzene sulfonyl bromide from the sodium salt of the sulfonic acid and phosphorus pentabromide, it was found that the reaction took a different course from that anticipated. Instead of the expected sulfonyl bromide, hexabromodiphenyl disulfide[2] was obtained. Further investigation showed that this reaction was quite general for salts of aromatic sulfonic acids.

The present work is an extension of this investigation to include the salts of the aliphatic sulfonic acids.

The sodium or potassium salts of methyl-, ethyl-, butyl-, isoamyl and benzylsulfonic acids, and the potassium salt of β-sulfo-β-phenylpropionic acid were prepared and treated with phosphorus bromides. In general this was carried out as follows: one mole of the salt was treated with one mole of phosphorus pentabromide (to form the sulfonyl bromide) and the reaction mixture was then further treated with two and one-half moles of phosphorus tribromide to bring about the reduction. In some cases this procedure was varied by allowing phosphorus pentabromide alone to react upon the sulfonate, and in one case the sulfonyl bromide was isolated and treated with phosphorus tribromide.

All the salts mentioned gave the corresponding disulfides when treated with *mixed* phosphorus bromides, except β-potassium sulfo-β-phenylpropionic acid, which gave β-bromo-β-phenylpropionic acid by the replacement of the SO_3K group by bromine as represented in the equations

$$C_6H_5CH(SO_3K)CH_2COOH + 2PBr_5 \longrightarrow C_6H_5CH(SO_2Br)CH_2COBr + 2POBr_3 + KBr + HBr$$

$$C_6H_5CH(SO_2Br)CH_2COBr + PBr_5 \longrightarrow C_6H_5CHBrCH_2COBr + SOBr_2 + POBr_3$$

This is similar to the action of phosphorus pentachloride on sulfonyl chlorides,[3] except that it takes place at a lower temperature.

When phosphorus pentabromide was used alone, in sufficient quantities to cause reduction to occur, according to the reaction postulated in the

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by B. E. Sorenson in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

[2] Kohlhase, THIS JOURNAL, **54**, 2441 (1932).

[3] Carius, *Ann.*, **114**, 142 (1860); Barbaglia and Kekulé, *Ber.*, **5**, 876 (1872).

first paper of this series,[2] the product isolated was usually the disulfide, but in some cases the sulfonyl bromide or the alkyl bromide resulted. Substitution of hydrogen by bromine also took place in several cases. Thus, β-potassium sulfo-β-phenylpropionic acid gave α,β-dibromophenylpropionic acid.

$$C_6H_5CH(SO_3K)CH_2COOH \xrightarrow{PBr_5} C_6H_5CHBrCHBrCOOH$$

The results are summarized in Table I.

TABLE I

RESULTS OBTAINED BY REDUCING VARIOUS ALIPHATIC SULFONATES AND SULFONYL BROMIDES WITH PHOSPHORUS BROMIDES

Reactant	Reagent	Product	Yield, %
CH_3SO_3K	$PBr_5 + PBr_3$	$(CH_3)_2S_2$	26
$C_2H_5SO_3K$	$PBr_5 + PBr_3$	$(C_2H_5)_2S_2$	54
$C_2H_5SO_3K$	PBr_5	$C_2H_5SO_2Br$	41
n-$C_4H_9SO_3K$	PBr_5 (1 mole)	n-$C_4H_9SO_3Br$	66
n-$C_4H_9SO_3K$	PBr_5 (3.5 moles)	$(n$-$C_4H_9)_2S_2$	49
n-$C_4H_9SO_3K$	$PBr_5 + PBr_3$	$(n$-$C_4H_9)_2S_2$	52
n-$C_4H_9SO_2Br$	PBr_3	$(n$-$C_4H_9)_2S_2$	63
iso-$C_5H_{11}SO_3Na$	$PBr_5 + PBr_3$	$(iso$-$C_5H_{11})_2S_2$	55
$C_6H_5CH_2SO_3Na$	$PBr_5 + PBr_3$	$(C_6H_5CH_2)_2S_2$	87
$C_6H_5CH_2SO_3Na$	PBr_5	$C_6H_5CH_2Br$	70
$C_6H_5CH(CO_2K)CH_2COOH$	$PBr_5 + PBr_3$	$C_6H_5CHBrCH_2COOH$	80
$C_6H_5CH(SO_3K)CH_2COOH$	PBr_5	$C_6H_5CHBrCHBrCOOH$	62

Experimental Part

Potassium Alkyl Sulfonates.—These were made by oxidizing the corresponding alkyl thiocyanates with nitric acid (sp. gr. 1.42).[4] The reaction mixtures were neutralized with potassium carbonate and evaporated to dryness. The crude potassium alkyl sulfonates so obtained were purified by recrystallizing from 95% alcohol.

TABLE II

PROPERTIES OF POTASSIUM ALKYL SULFONATES

		Analyses, %					
		Calcd.		Found			
Sulfonate	Yield, %	K	S	K		S	
Methyl	90						
Ethyl	80						
n-Butyl	70	22.19	18.21	22.05	22.06	18.55	18.42
Isoamyl[a]	41	13.22 (Na)	18.41	13.19	13.10	18.78	18.90

[a] The sodium salt was made by oxidizing 50 g. of isoamyl disulfide with 20 cc. of nitric acid (sp. gr. 1.42).

Alkyl Sulfonyl Bromides.—One-tenth mole of potassium alkyl sulfonate and 0.35 mole of phosphorus pentabromide were heated for forty minutes at 70–80°, poured into 400 g. of crushed ice and stirred continuously until about 60 cc. of clear liquid remained undissolved. The lower layer was separated and shaken in a separatory funnel with 200 g. of ice for two minutes. The lower layer was separated, dried with calcium chloride and fractionated.

[4] Muspratt, *Ann.*, **65**, 261 (1848).

TABLE III

PROPERTIES OF ALKYL SULFONYL BROMIDES

Sulfonyl bromide	Yield, %	Boiling point, °C.	d_4^{25}	Analyses, % Calcd. S	Calcd. Br	Found, S	S	Br	Br	M. p. of sulfonamide, °C.
Ethyl[a]	41	103–106 (40 mm.)[b]		18.50		20.44	20.30			57–58
n-Butyl	66	101–102 (11 mm.)	1.5109	15.94	39.75	15.58	15.51	40.03	39.93	

[a] *J. prakt. Chem.*, [2] **26**, 384 (1880).

[b] Cherbuliez and Schnauder [*Helv. Chim. Acta*, **6**, 249 (1923)] give 80° (13 mm.).

Alkyl Disulfides.—One-third mole of finely ground potassium alkyl sulfonate was mixed with 0.33 mole of phosphorus pentabromide, after which the reaction flask was fitted with a calcium chloride tube and heated on a steam-bath for fifteen minutes. After cooling to 80°, 0.8 mole of phosphorus tribromide was added and the temperature maintained at 70–80° for forty minutes. The red reaction mixture was transferred to a 1-liter flask, cooled in an ice-bath and dissolved in 250 cc. of ether. The halides of phosphorus were hydrolyzed by adding water slowly until the ether formed a separate layer, and then the solution was steam distilled. The ether layer of the distillate was separated, washed once with water, then with 5% sodium carbonate solution and finally with water. After drying with calcium chloride, it was filtered and fractionated, using a Clarke flask with column attached.

TABLE IV

PROPERTIES OF ALKYL DISULFIDES

Disulfide	Yield, %	Boiling point, °C.	$d_4^{X°}$	Analyses Sulfur Calcd.	Found		$AgNO_3$ double salt Ag, calcd.	Ag, found	
Methyl	26	108–108.5 (748 mm.)[a]	1.0606 (16°)	68.08	68.54	68.43	40.87	40.69	40.84
Ethyl	54	151–152 (736 mm.)[b]	0.9961 (20°)[b]	52.47	52.96	52.89	38.95	37.01	36.88
n-Butyl[c]	52	227–229 (735 mm.)	.9327 (25°)	35.95	36.63	36.57			
Isoamyl	55	123.5–124 (12 mm.)	.9188 (18°)[d]	31.08	31.73	31.68			
Benzyl	87	(m. p. 70–71.5°)[e]		26.06	26.87	26.75			

[a] Pierre [*Ann.*, **80**, 128 (1830)] gives 112.1 (744 mm.). [b] Wasini [*Ber.*, **15**, 2882 (1882)] gives b. p. 152.8–153.4° (corr.); d_4^{20} 0.9927. [c] Phosphorus pentabromide alone gave 49%, b. p. 224–233°. Phosphorus tribromide alone gave 63%. [d] Henry [*Jahresb.*, **48**, 699 (1847)] gives d_4^{18} 0.918. [e] Hofmann [*Ber.*, **20**, 15 (1887)] gives 71–72°.

Preparation of *n*-Butyl Disulfide by a Known Method.—Since *n*-butyl disulfide was not described in the literature, it was made by refluxing an alcoholic solution of sodium disulfide with *n*-butyl chloride. The alcohol and excess butyl chloride were distilled off at atmospheric pressure and enough water added to dissolve the sodium chloride. The oily upper layer was separated, dried and fractionated at reduced pressure. *n*-Butyl disulfide was water white and had the following properties: b. p. 93–94° (7 mm.) or 226–229° (740 mm.), d_4^{25} 0.9329.

Anal. Calcd. for $C_8H_{18}S_2$: S, 35.95. Found: S, 36.64, 36.50.

n-Butyl trisulfide, the by-product, was pale yellow and had the following properties: b. p. 119–121° (6 mm.) and d_4^{25} 1.0117.

Anal. Calcd. for $C_8H_{18}S_3$: S, 45.73. Found: S, 46.50, 46.62.

Preparation of Benzyl Bromide from Sodium Benzyl Sulfonate.—Benzyl bromide was obtained in 70% yield when fifteen grams of sodium benzyl sulfonate and 93 g. of phosphorus pentabromide were heated at 85–90° for fifteen minutes. The mixture,

which fused and gave off hydrogen bromide, was dissolved in 100 cc. of ether, and water was added until the ether layer separated. The ether solution was separated, washed once with water and dried with calcium chloride. After evaporating the ether, the residual liquid was fractionated at 18 mm., and redistilled at atmospheric pressure; b. p. 195–197° (740 mm.).

Anal. Calcd. for C_7H_7Br: Br, 46.73. Found: Br, 48.64, 48.33.

Preparation of β-Bromo-β-phenylpropionic Acid.—Eighteen grams of β-potassium sulfo-β-phenylpropionic acid (made from cinnamic acid and potassium sulfite by the method of Valet [*Ann.*, **154**, 63 (1870)] and purified by washing with benzene and recrystallizing from alcohol), 58 g. of phosphorus pentabromide and 45 g. of phosphorus tribromide were heated at 85–90° with occasional shaking until the phosphorus pentabromide was dissolved. The reaction mixture was cooled and dissolved in 125 cc. of ether. The ether solution was treated with water to hydrolyze the phosphorus bromides, dried, filtered and evaporated to dryness. This gave 12 g. (80%) of crude gray β-bromo-β-phenylpropionic acid, which was crystallized twice from benzene to give a colorless material, m. p. 135–137°. An authentic sample of β-bromo-β-phenylpropionic acid melted at 137°; mixed m. p. 135.5–137°.[5]

Preparation of α,β-Dibromo-β-phenylpropionic Acid.—Nineteen grams of β-potassium sulfo-β-phenylpropionic acid and 125 g. of phosphorus pentabromide were mixed and heated at 100° until the evolution of hydrogen bromide ceased (about one hour). The reaction product was isolated in the same way as the β-bromo-β-phenylpropionic acid. The crude product was crystallized once from benzene, giving 13.2 g. (62%) of α,β-dibromo-β-phenylpropionic acid, m. p. 188–195° (with decomposition). It was recrystallized and melted at 197° (when heated rapidly near the melting point).[6]

Anal. Calcd. for $C_9H_8O_2Br_2$: Br, 51.94. Found: Br, 51.60, 51.80.

Summary

1. Several salts of aliphatic sulfonic acids were reduced to the corresponding disulfides with a mixture of phosphorus pentabromide and phosphorus tribromide.

2. Phosphorus pentabromide alone gave the same disulfides in some cases. In other cases the sulfonic acid group was replaced by bromine.

3. The sulfonyl bromide group is more easily replaced by bromine (by means of phosphorus pentabromide) when attached to an aliphatic radical than when attached to an aromatic nucleus.

4. The presence of a phenyl radical on the carbon holding the sulfonyl bromide group facilitates the replacement of the latter by bromine.

MINNEAPOLIS, MINNESOTA

[5] Bodwig, *Ber.*, **12**, 538 (1874).

[6] Sudborough and Thompson [*J. Chem. Soc.*, **83**, 670 (1903)] give the melting point as 197° (when heated rapidly).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE MECHANISM OF THE REDUCTION OF SULFONYL BROMIDES WITH PHOSPHORUS TRIBROMIDE[1]

BY W. H. HUNTER AND B. E. SORENSON

RECEIVED APRIL 18, 1932 PUBLISHED AUGUST 5, 1932

Kohlhase[2] discovered that many aromatic sulfonyl bromides could be easily and conveniently reduced to disulfides by phosphorus tribromide. Hunter and Sorenson[3] showed that the reaction could be applied with equal success to sulfonyl bromides of the aliphatic series. These earlier papers were concerned largely with the preparative aspects of the new reaction. Attention was logically next devoted to the mechanism of the change.

In order to elucidate the mechanism of the reaction, two methods of attack are possible: attempts could be made to isolate intermediate products of the reduction, or possible intermediate products could be synthesized by other means, and the action of phosphorus bromides upon these substances studied. Since the first procedure is attended with great difficulty and uncertainty under the conditions necessary for these reductions, we chose the latter method of attack.

For this purpose it was first assumed that the reaction took place in steps which might be represented as

$$RSO_2Br + PBr_3 \longrightarrow RSOBr + POBr_3 \quad (1)$$
$$RSOBr + PBr_3 \longrightarrow RSBr + POBr_3 \quad (2)$$
$$2RSBr + PBr_3 \longrightarrow RSSR + PBr_5 \quad (3)$$

Examples of each of these possible intermediate products were prepared and subjected to the action of phosphorus tribromide as described in this paper.

No sulfinyl bromides were described in the literature; therefore, *p*-toluene sulfinyl chloride[4] was chosen for the first experiments. This sulfinyl chloride was reduced very readily by phosphorus tribromide, although it gave a slightly lower yield of *p*-toluene disulfide than *p*-toluene sulfonyl bromide which was also reduced as a control.[5]

[1] This article is an abstract of part of a thesis submitted by B. E. Sorenson to the Faculty of the Graduate School of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

[2] Kohlhase, THIS JOURNAL, **54**, 2441 (1932).

[3] Hunter and Sorenson, *ibid.*, **54**, 3364 (1932).

[4] Hilditch and Smiles, *Ber.*, **41**, 4115 (1908).

[5] The comparison between the *p*-toluene sulfinyl chloride and the sulfonyl bromide was not entirely logical, but since previous work[2] has shown that sulfonyl chlorides are not reduced by phosphorus tribromide whereas sulfonyl bromides are readily reduced, it seems probable that the sulfinyl bromide would be reduced at least as easily as the sulfinyl chloride.

Otto and Rössing[6] also found that sodium benzene sulfinate was reduced to the disulfide by phosphorus trichloride according to the equation

$$6C_6H_5SO_2Na + 9PCl_3 \longrightarrow 3(C_6H_5S)_2 + 3NaCl + 8POCl_3 + Na_3PO_4$$

If the first product of this reaction is the sulfinyl chloride it indicates that this is reduced by the phosphorus trichloride. Since sulfonyl bromides are not reduced by phosphorus trichloride,[2] this can be adduced as further evidence that sulfinyl bromides are more easily reduced than sulfonyl chlorides. This ease of reduction of the sulfinyl bromides very likely accounts for the fact that sulfinyl bromides do not appear as intermediate products.

o-Nitrophenyl sulfur bromide[7] was chosen for the next experiments as it was well known and quite stable. This sulfur bromide did not react rapidly with phosphorus tribromide. However, when it was allowed to stand for several days in dry ether with phosphorus tribromide it gave some *o*-nitrophenyl disulfide. Under similar conditions the sulfur bromide alone in dry ether also gave some *o*-nitrophenyl disulfide but not as much as when phosphorus tribromide was present. These phenomena may be explained by assuming that the sulfur bromide dissociates reversibly into bromine and the disulfide, and that phosphorus tribromide may upset the equilibrium by combining with the bromine thus liberated.

$$2RSBr \rightleftharpoons RSSR + Br_2$$
$$Br_2 + PBr_3 \rightleftharpoons PBr_5$$

When *o*-nitrophenyl disulfide was treated with an excess of phosphorus pentabromide, *o*-nitrophenyl sulfur bromide was formed, thus proving that the above reaction is in fact reversible. An attempt was made to prepare tribromobenzene sulfur bromide from the disulfide and bromine according to the general method of Zincke and Farr[7] but it could not be isolated. As soon as the solvent and excess bromine were removed the reaction was completely reversed to give back the disulfide.

o-Nitrophenylsulfonyl bromide was reduced by phosphorus tribromide at low temperatures. The products were the disulfide and the sulfur bromide when the reaction products were isolated in the absence of water. When the reaction mixture was dissolved in ether and hydrolyzed by adding water, *o*-nitrophenyl disulfide and *o*-nitrothiophenol were obtained.

Thionaphthol[2] was previously isolated in this type of reduction and was assumed to be formed in accordance with the equations

$$RSSR + PBr_3 \rightleftharpoons (RS)_2 \cdot PBr_3$$
$$RSSR \cdot PBr_3 + 4H_2O \longrightarrow 2RSH + 3HBr + H_3PO_4$$

This mechanism was tested by mixing *o*-nitrophenyl disulfide and phosphorus tribromide, but no thiophenol resulted. The next postulate was

[6] Otto and Rössing, *Ber.*, **24**, 3883 (1891).

[7] Zincke and Farr, *Ann.*, **391**, 67 (1912).

that the thiophenol resulted from the further reduction of the sulfur bromide when water was added to the ether solution. However, none of the reducing agents present in the reaction mixture, such as phosphorus acid and hydrobromic acid, reduced the sulfur bromide to the thiophenol in the presence of water and ether. However, pure *o*-nitrophenyl sulfur bromide and phosphorus tribromide in ether solution gave almost a quantitative yield of thiophenol when water was added. From this it was concluded that the thiophenol resulted from the hydrolysis of a molecular compound first formed from the sulfur bromide and phosphorus tribromide.

$$RSBr + PBr_3 \rightleftharpoons RSPBr_4 \xrightarrow{H_2O} RSH + POBr_3 + HBr$$

A freezing point method was devised to determine if evidence of the formation of a molecular compound could be obtained. Phosphorus tribromide or *o*-nitrophenyl sulfur bromide alone gave normal freezing point depressions in benzene. Likewise, the mixture gave a normal freezing point depression in benzene showing that no molecular compound was formed in this solvent. However, when a solution of the two in *benzene* was hydrolyzed (as was done with the ether solution) *o*-nitrophenyl disulfide was formed instead of the thiophenol obtained in ether. No direct proof of the presence of a molecular compound in the ether solution could be observed, but the different results obtained in ether and in benzene strengthened our opinion that some such explanation was probably correct.

On the basis of all the evidence we are able to postulate definitely that the steps in the reduction of sulfonyl bromides to disulfides are the following:

$$RSO_2Br + PBr_3 \longrightarrow RSOBr + POBr_3 \quad (1)$$

$$RSOBr + PBr_3 \longrightarrow RSBr + POBr_3 \quad (2)$$

$$2RSBr \rightleftharpoons RSSR + Br_2 \quad (3)$$

$$Br_2 + PBr_3 \rightleftharpoons PBr_5 \quad (4)$$

$$RSBr + PBr_3 \xrightleftharpoons{\text{ether}} RSPBr_4 \quad (5)$$

$$RSPBr_4 + 4H_2O \longrightarrow 2RSH + 2H_3PO_4 + 4HBr \quad (6)$$

Experimental

Preparation of *p*-Toluenesulfinyl Chloride.—*p*-Toluenesulfinyl chloride was made by treating *p*-toluenesulfinic acid with an excess of thionyl chloride according to the method of Hilditch and Smiles.[8] The material obtained was a liquid at room temperature. The above authors give the melting point as 54–58°.

Reaction between *p*-Toluenesulfinyl Chloride and Phosphorus Tribromide.—(a) Four grams (1 mole) of *p*-toluenesulfinyl chloride and 10 g. (1.5 moles) of phosphorus tribromide were mixed in a 50-cc. flask. The mixture became so hot that free bromine was given off and phosphorus pentabromide sublimed on the neck of the flask. When the reaction mixture became cool it was dissolved in 30 cc. of ether and water was added to hydrolyze the halides of phosphorus. The ether layer was separated, washed with sodium carbonate solution and dried. The ether was evaporated and the residual red oil allowed to solidify. This gave 1.5 g. (54% of the theoretical quantity) of crude *p*-

[8] Ref. 4, p. 4114.

toluene disulfide. This was crystallized from alcohol and gave a colorless product of m. p. 44–45°. *p*-Toluene disulfide melts at 46°.[9]

Anal. Subs., 0.1190: $BaSO_4$ (Carius) 0.2308. Calcd. for $C_{14}H_{14}S_2$: S, 26.06. Found: S, 26.62.

Reaction between *p*-Toluenesulfonyl Bromide and Phosphorus Tribromide.—Three grams (1 mole) of *p*-toluenesulfonyl bromide[10] was heated with 8.7 g. (2.5 moles) of phosphorus tribromide at 80–90° for twenty minutes. The *p*-toluene disulfide was isolated as in the previous experiment, and weighed 0.9 g. (56% of the theoretical). The recrystallized disulfide melted at 44–45°, and showed no depression when mixed with a sample prepared as in the previous experiment.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Sulfur Bromide in Ether.—One-half gram of *o*-nitrophenyl sulfur bromide was dissolved in 20 cc. of dry ether. To this 2.8 g. of phosphorus tribromide was added. The flask was stoppered and allowed to stand for five days. After several hours the solution became cloudy and in about eight hours a precipitate began to separate. This was filtered off after twenty-four hours and washed with benzene to remove a small amount of a green amorphous material. The disulfide weighed 0.05 g. (15%), m. p. 193–194°; mixed melting point with known *o*-nitrophenyl disulfide, 193–194.5°. The known disulfide melted at 195°. In a check experiment a yield of 5% of the disulfide was obtained.

The Action of Phosphorus Pentabromide on *o*-Nitrophenyl Disulfide in Dry Ether.—In a flask were placed 2 g. (1 mole) of *o*-nitrophenyl disulfide, 7 g. (3 moles) of phosphorus pentabromide and 50 cc. of dry ether. The *o*-nitrophenyl disulfide dissolved completely after about two hours. The ether solution was decanted from a small amount of a heavy red oil and evaporated at reduced pressure until a precipitate started to form. It was then treated with 50 cc. of ligroin and stirred until the precipitate was pale yellow. The solution was filtered and the precipitate washed several times with petroleum ether and dried. There resulted 1.2 g. (40%) of *o*-nitrophenyl sulfur bromide. The product melted at 78–81° after crystallization from benzine. Mixed with known *o*-nitrophenyl sulfur bromide it melted at 78–83°. The known product melted at 83–84°.

Attempt to Prepare Tribromophenyl Sulfur Bromide from Hexabromodiphenyl Disulfide and Bromine.—2.7 g. of hexabromodiphenyl disulfide was suspended in a mixture of 20 cc. of carbon tetrachloride and 4 cc. of bromine. The disulfide dissolved slowly and after twelve hours was all in solution. The carbon tetrachloride was evaporated in a vacuum desiccator. The solid which remained melted at 215–217°. The original disulfide melted at 215–217°; mixed m. p. 215–217°.

Preparation of *o*-Nitrophenylsulfonyl Bromide.—This compound was prepared by a modification of the process of Zincke and Farr[7] for the preparation of sulfonyl chlorides.

Fifteen grams of *o*-nitrophenyl disulfide was suspended in 100 cc. of glacial acetic acid. To this was added 20 cc. of bromine dissolved in 100 cc. of glacial acetic acid. The mixture was heated at 50–60° until the disulfide dissolved. Water was added slowly until the total volume of the solution was about 500 cc. If the first addition of water caused a yellow bulky precipitate to form, it was necessary to heat the reaction mixture until this redissolved. The crude sulfonyl bromide which separated as a pink or colorless precipitate was filtered off, washed with water and dissolved in a small amount of ether without drying. The water was separated from the ether solution and after concentrating the ether to a volume of 35 cc. the sulfonyl bromide was precipitated by adding ligroin. The sulfonyl bromide was filtered off, washed once with ligroin and dried. The yield was 20 g. (79%); m. p. 62.5–63.5°. Recrystallized once from equal parts of benzene and benzine, a colorless product was obtained, m. p. 63–64° (uncorr.).

[9] *J. prakt. Chem.*, [2] **41**, 190 (1890).

[10] Otto, *Ann.*, **142**, 98 (1867).

Anal. Subs., 0.2488, 0.2215: AgBr (Carius), 0.1766, 0.1560. Calcd. for $C_6H_4O_4NBrS$: Br, 30.04. Found: Br, 30.24, 29.97.

For further identification, the sulfonyl bromide was converted to the sulfonamide by saturating a ligroin–benzine solution with dry ammonia. The amide melted at 190.5–191.5° after recrystallizing from water. *o*-Nitrophenylsulfonamide[11] melts at 190–191°.

The Action of Phosphorus Tribromide on *o*-Nitrophenylsulfonyl Bromide.—Three grams (1 mole) of *o*-nitrophenylsulfonyl bromide was placed in a 100-cc. flask fitted with a dropping funnel. The flask was cooled in an ice-bath and 7.6 g. (2.5 moles) of phosphorus tribromide was added slowly through the dropping funnel. The reaction mixture was then agitated with 20 cc. of ligroin until only a flocculent yellow precipitate and a small amount of tarry material on the bottom of the flask remained undissolved. The crude yellow *o*-nitrophenyl sulfur bromide was filtered and the tar extracted with hot benzene. The crude sulfur bromide was crystallized from benzine and gave 1.1 g., m. p. 79–82°; mixed m. p. with known *o*-nitrophenyl sulfur bromide (m. p. 83–84°) was 80–83°.

Anal. Subs., 0.1242, 0.1214: AgBr (Carius), 0.0985, 0.0963. Calcd. for $C_6H_4O_3NBrS$: Br, 34.14. Found: Br, 33.68, 33.75.

The residue which did not dissolve in the benzine in the second crystallization was extracted with the benzene used to extract the original residue in the flask. The solution was filtered and evaporated to a volume of 4 cc. The precipitate which formed on cooling was filtered, washed with dilute sodium hydroxide solution and dried. There was obtained 0.3 g. of crude *o*-nitrophenyl disulfide. It was recrystallized from benzene and melted at 192.5–193.5°. *o*-Nitrophenyl disulfide[12] melts at 195°. Mixed with known disulfide it melted at 193–194°.

If instead of isolating the reaction products as described above, the reaction mixture was dissolved in ether and hydrolyzed by adding water slowly, the products were *o*-nitrothiophenol and *o*-nitrophenyl disulfide. These were separated by extracting with normal sodium hydroxide solution. After filtration the thiophenol was reprecipitated by adding dilute hydrochloric acid. The crude disulfide was purified by recrystallizing from benzene. The *o*-nitrophenyl disulfide melted at 194–195°. The *o*-nitrothiophenol melted at 54–55°. Mixed with known *o*-nitrothiophenol (m. p. 56–56.5°) it melted at 54–55°.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Disulfide in Ether.—One gram of *o*-nitrophenyl disulfide was suspended in 15 cc. of ether. To this was added 3 cc. of phosphorus tribromide. The phosphorus tribromide was hydrolyzed by adding water slowly without cooling. When 15 cc. of water had been added the mixture was allowed to stand at room temperature until the ether evaporated. The precipitate which resulted was filtered off, washed with water and dried. This gave 0.95 g. of *o*-nitrophenyl disulfide, m. p. 194–195°. The original disulfide melted at the same temperature.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Sulfur Bromide in Ether and in Benzene.—(*a*) **In ether:** 0.5 g. of *o*-nitrophenyl sulfur bromide was dissolved in 2.8 g. of phosphorus tribromide. The solution was diluted with 10 cc. of ether; 10 cc. of water was added to the ether solution drop by drop without cooling, and the mixture was allowed to stand until the ether layer evaporated. The crystals which formed were filtered, washed with cold water and dried. This gave 0.3 g. (93%) of crude *o*-nitrothiophenol; m. p. 49–51°. It was dissolved in normal sodium hydroxide solution,

[11] Ekbom, *Ber.*, **35**, 657 (1902).

[12] Wohlfahrt, *J. prakt. Chem.*, **66**, 553 (1902).

reprecipitated with hydrochloric acid, filtered, washed with water and dried. The purified thiophenol melted at 56–56.5°. *o*-Nitrothiophenol[13] melts at 56°.

Anal. Subs. 0.1415: $BaSO_4$, 0.2070. Calcd. for $C_6H_5O_2NS$: S, 20.20. Found: S, 20.09.

(*b*) **In Benzene:** One-half gram of *o*-nitrophenyl sulfur bromide was dissolved in 2.8 g. of phosphorus tribromide. To this 10 cc. of benzene was added. The reaction mixture was hydrolyzed as in part (*a*). The crystals formed were stirred with sodium hydroxide solution, filtered, washed with water and dried. This gave 0.25 g. (92% of theoretical) of *o*-nitrophenyl disulfide; m. p. 192–194°; no depression when mixed with known *o*-nitrophenyldisulfide (m. p. 195°). The sodium hydroxide filtrate was acidified with hydrochloric acid but no *o*-nitrothiophenol separated.

Determination of Freezing Points

***o*-Nitrophenyl Sulfur Bromide in Benzene.**—Sample 0.4995; benzene 17.40; depression 0.600°. Calcd. for $C_6H_4O_2NBrS$: mol. wt. 234. Found: 239.

Phosphorus Tribromide and *o*-Nitrophenyl Sulfur Bromide in Benzene.—The experiment was carried out in the same way as molecular weight determinations by the cryoscopic method. The phosphorus tribromide was added to the benzene first and the freezing point depression noted. An equivalent weight of *o*-nitrophenyl sulfur bromide was added to this in three portions and the freezing point observed after each addition.

Substance added	Freezing point, °C.
Pure benzene	4.920
0.5920 g. phosphorus tribromide	4.306
0.1280 g. *o*-nitrophenyl sulfur bromide	4.147
0.3840 g. *o*-nitrophenyl sulfur bromide	3.835
0.5120 g. *o*-nitrophenyl sulfur bromide	3.688

Depression due to phosphorus tribromide 0.614°

Depression due to *o*-nitrophenyl sulfur bromide 0.618°

Calcd. mol. wt. of PBr_3: 271. Found: 277. Calcd. mol. wt. of $C_6H_4O_2NBrS$: 234. Found: 233.

Summary

1. *p*-Toluene-sulfinyl chloride was reduced readily to *p*-toluene disulfide by phosphorus tribromide.

2. *o*-Nitrophenyl sulfur bromide was slowly reduced by phosphorus tribromide to give the corresponding disulfide in poor yield. The presence of phosphorus tribromide increased the yield of disulfide.

3. Phosphorus pentabromide reacted with *o*-nitrophenyl disulfide to give *o*-nitrophenyl sulfur bromide.

4. *o*-Nitrophenyl sulfonyl bromide was reduced to *o*-nitrophenyl sulfur bromide by phosphorus tribromide.

5. The action of water on an ether solution of *o*-nitrophenyl sulfur bromide and phosphorus bromide gave *o*-nitrothiophenol.

6. It is therefore postulated that the course of the reduction of a sulfonyl bromide by phosphorus tribromide is as follows: sulfonyl bromide $\rightarrow$ sulfinyl bromide $\longrightarrow$ sulfur bromide $\rightleftarrows$ disulfide + Br_2. Sulfur

[13] Mayer, *Ber.*, **42**, 3059 (1909).

bromide + PBr_3 (in ether) ⟶ addition compound ⟶ thiophenol (on hydrolysis).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION NO. 209 FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE HYDROLYSIS OF LIGNIN WITH 12% HYDROCHLORIC ACID

BY MAX PHILLIPS AND M. J. GOSS

RECEIVED APRIL 20, 1932 PUBLISHED AUGUST 5, 1932

Hägglund and Björkman[1] and later Hägglund and Rosenqvist[2] distilled lignin (isolated by the fuming hydrochloric acid method) with 12% hydrochloric acid and obtained a distillate which gave a precipitate with phloroglucinol, barbituric acid and with thiobarbituric acid. The substance present in the distillate was not definitely identified, but was shown to be neither furfural, methylfurfural nor hydroxymethylfurfural.

Freudenberg and Harder[3] distilled lignin (isolated from wood by a method similar to that used by Urban[4]) with 12% hydrochloric acid and identified the volatile hydrolytic product as formaldehyde. In a subsequent paper, Freudenberg, Harder and Markert[5] advanced the hypothesis that the formaldehyde arises from a methylene dioxide group (—O—CH_2—O—) present in the lignin molecule, as compounds containing the methylene dioxide group are known to yield formaldehyde when they are distilled with hydrochloric acid. However, this interpretation of the reaction involved has been questioned by Fuchs and Horn.[6] They distilled with hydrochloric acid lignin, acetylated lignin and two oxidized acetylated lignin preparations and found that lignin itself gave a greater yield of formaldehyde–barbituric acid condensation product than the other three modified lignin preparations.

The present investigation was undertaken for the purpose of determining (1) whether lignin isolated from materials other than wood gives formaldehyde when distilled with 12% hydrochloric acid, and (2) whether the method employed for the isolation of the lignin has any effect on the formaldehyde-yielding component presumably present in lignin.

Experimental

The lignin used in these experiments was isolated from three different sources by the following different methods. The lignin was isolated from corn cobs by the alco-

[1] Hägglund and Björkman, *Biochem. Z.*, **147**, 74 (1924).

[2] Hägglund and Rosenqvist, *ibid.*, **179**, 376 (1926).

[3] Freudenberg and Harder, *Ber.*, **60**, 581 (1927).

[4] Urban, *Cellulosechem.*, **7**, 73 (1926).

[5] Freudenberg, Harder and Markert, *Ber.*, **61**, 1760 (1928).

[6] Fuchs and Horn, *Ber.*, **62**, 2647 (1929).

holic[7] and aqueous sodium hydroxide[8] methods, by the fuming hydrochloric acid method of Willstätter and Zechmeister[9] and by Urban's method[4] as modified by Freudenberg and Harder.[10] The lignin from oat hulls was isolated by the alcoholic and aqueous sodium hydroxide methods,[11] by the method of Willstätter and Zechmeister[9] and by Freudenberg and Harder's modification[10] of Urban's method. The lignin from spruce wood was prepared by the aqueous sodium hydroxide method and according to the procedure of Freudenberg and Harder.[10]

Distillation of the Lignin with 12% Hydrochloric Acid.—The distillation of the lignin with the 12% hydrochloric acid was carried out exactly as in the determination of pentosans by Tollens' method, as described in the official book of methods of the Association of Official Agricultural Chemists.[12] In all experiments, three grams of lignin was used for each distillation. The distillate was made up with water to a volume of 500 cc. in a volumetric flask. A portion of this solution was tested immediately for formaldehyde by the Schryver[13] modification of the Rimini[14] test. This test is specific for formaldehyde. Furfural, which might be expected to be present in some of the distillates, gives no reaction with the reagents employed in the formaldehyde test when the dilution reaches 1:100,000. When the concentration of the furfural is approximately 1:1000, or greater, an apricot-yellow color is formed which on addition of concentrated hydrochloric acid turns green and rapidly disappears. Formaldehyde, on the other hand, gives a fuchsin-like color which is quite permanent.

TABLE I

HYDROLYSIS OF LIGNIN WITH 12% HYDROCHLORIC ACID

Source of lignin	Method for isolation of lignin	Formaldehyde in distillate: Qualitative test for[a]	Formaldehyde in distillate: Calcd. on wt. of lignin used, %	Furfural (Qualitative test with aniline acetate paper)[a]
Corn cobs	Alcoholic sodium hydroxide	−	..	−
Corn cobs	Aqueous sodium hydroxide	−	..	−
Corn cobs	Willstätter and Zechmeister	−	..	+
Corn cobs	Urban's, modified by Freudenberg and Harder	−	..	Trace
Oat hulls	Alcoholic sodium hydroxide	−	..	−
Oat hulls	Aqueous sodium hydroxide	−	..	−
Oat hulls	Willstätter and Zechmeister	Trace	..	+
Oat hulls	Urban's, modified by Freudenberg and Harder	+	0.61	−
Spruce wood	Aqueous sodium hydroxide	−	..	+
Spruce wood	Urban's, modified by Freudenberg and Harder	+	0.79	−

[a] −, Test was negative; +, test was positive.

[7] Phillips, THIS JOURNAL, **49**, 2037 (1927).

[8] Phillips, *ibid.*, **51**, 2421 (1929).

[9] Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

[10] Ref. 3, page 583.

[11] Phillips, THIS JOURNAL, **52**, 793 (1930).

[12] "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Association of Official Agricultural Chemists, Washington, D. C., 1925.

[13] Schryver, *Proc. Roy. Soc.* (*London*), **82B**, 226 (1910).

[14] Rimini, *Bull. Soc. Chim. France*, [3] **20**, 896 (1898).

The formaldehyde in the distillates was determined quantitatively by the iodine titration method.[15] The results obtained are given in Table I.

It will be observed from Table I that formaldehyde was obtained in appreciable quantity in the distillates from only two of the eight lignin preparations, namely, in that of the lignin from oat hulls prepared by the Freudenberg and Harder modification of Urban's method, and in the distillate of the lignin from spruce wood prepared by the same method. In the distillates from all the other lignin preparations, except one, no formaldehyde could be detected. In the distillate of the lignin from oat hulls prepared by the method of Willstätter and Zechmeister, the test for formaldehyde was so slight that it can be characterized only as a "trace." The percentage formaldehyde obtained from the lignin of spruce wood is in substantial agreement with that recorded by Freudenberg and Harder.[16]

It would appear from the data that the source of the lignin and the method employed for its isolation from the lignified plant materials are two factors which determine whether formaldehyde is obtained as an hydrolytic degradation product from lignin. Thus, lignin from oat hulls prepared by Freudenberg and Harder's modification of Urban's method, when hydrolyzed with 12% hydrochloric acid, yielded a quantity of formaldehyde equivalent to 0.61% of the weight of the lignin, whereas lignin isolated from corn cobs by the same method gave absolutely no test for formaldehyde when similarly hydrolyzed. On the other hand, the hydrolysate of the lignin from oat hulls prepared by the alcoholic sodium hydroxide method gave no test for formaldehyde and that from the lignin isolated from the same source by the method of Willstätter and Zechmeister contained only a trace of formaldehyde. The hydrolysate from the last-mentioned lignin preparation, however, gave a positive test for furfural so that in this case the minute quantity of formaldehyde may have originated from some carbohydrate impurity.

If we were to accept the explanation of Freudenberg, Harder and Markert[5] that the formaldehyde arises from a methylene dioxide group present in the lignin molecule, the conclusion would have to be drawn that this group is present only in lignin isolated from certain plant materials. Furthermore, it is rather difficult to conceive how such a mild treatment as that employed in the isolation of lignin by the alcoholic sodium hydroxide method could bring about the removal of such a comparatively stable group as the methylene dioxide group. In this connection, attention is called to the fact that no formaldehyde was found in the distillate from the lignin fraction isolated from oat hulls by the alcoholic sodium hydroxide method, whereas in the distillate from the lignin isolated from the same source by Freudenberg and Harder's modification of Urban's method (where a solution comprising concentrated hydrochloric acid and sirupy phosphoric acid is employed for the removal of the cellulose and other carbohydrates) formaldehyde was obtained to the extent of 0.61% of the weight of the lignin. It would seem therefore, questionable whether the formaldehyde that is obtained in the hydrolysis of certain lignin preparations can be considered as a fission product of a methylene dioxide group.

Summary

Lignin isolated from corn cobs, oat hulls and spruce wood by the method of Willstätter and Zechmeister, by the alcoholic and aqueous sodium hydroxide methods and by Freudenberg's modification of Urban's method, was distilled with 12% hydrochloric acid. Formaldehyde was obtained in appreciable quantity only in the distillate from the lignin isolated from oat

[15] Smith, THIS JOURNAL, **25**, 1028 (1903).

[16] Ref. 3, page 585.

hulls by the Freudenberg and Harder modification of Urban's method, and in the distillate of the lignin from spruce wood prepared by the same method. The result so far as the lignin from spruce wood is concerned is in agreement with that recorded by Freudenberg and Harder.

The results obtained are discussed from the standpoint of the probable presence of the methylene dioxide group in the lignin molecule.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. XXIII. THE STRUCTURE OF ROTENONONE

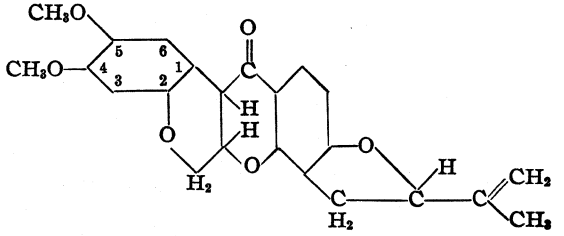
BY F. B. LAFORGE

RECEIVED APRIL 21, 1932 PUBLISHED AUGUST 5, 1932

Rotenonone is obtained from rotenone by chromic acid oxidation, or by the action of nitrous acid. Butenandt assumed the compound to be a 1,2-diketone of formula $C_{23}H_{20}O_7$ arising from the oxidation of a methylene group adjacent to the carbonyl group present in rotenone. It is converted by the action of strong alkali, with the addition of one mole of water, into an acid of the supposed formula $C_{23}H_{22}O_8$, a reaction which was interpreted by Butenandt as a benzilic acid rearrangement.[1]

In a previous article[2] we have shown that the analogs of rotenonone are obtained not only from dihydrorotenone, isorotenone and rotenonic acid, but even more readily from the corresponding dehydro derivatives and that all derivatives of the rotenonone type belong to the dehydro series. Therefore rotenonone should be represented by the formula $C_{23}H_{18}O_7$, rotenononic acid by $C_{23}H_{20}O_8$, and corresponding formulas should be applied to the other derivatives. These formulas in fact correspond more closely to the analytical figures obtained for the respective compounds.

After the complete formula for rotenone (I) had been established,[3]



I

it became evident that the formula for rotenonone proposed by Butenandt was untenable.

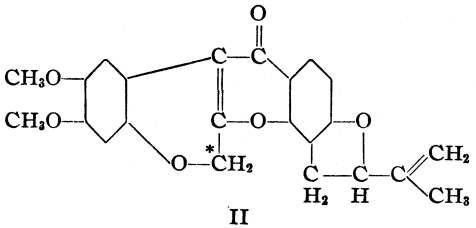
[1] Butenandt, *Ann.*, **464**, 253 (1929).

[2] LaForge and Smith, THIS JOURNAL, **52**, 1091 (1930).

[3] LaForge and Haller, *ibid.*, **54**, 810 (1932).

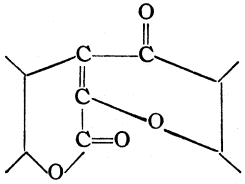
In a previous article[4] we have described the oxidation of dihydrorotenononic acid to dihydrotubaic acid, and also the reconversion of dihydrorotenononic acid to dihydrorotenonone. The last-mentioned reaction is best explained by the assumption that dihydrorotenonone and hence rotenonone are lactones.

It is apparent from consideration of the formula of dehydrorotenone II

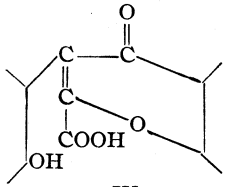


II

that a lactone would be formed on oxidation of the methylene group indicated by the asterisk. Consequently rotenonone would be represented by the formula III and rotenononic acid by IV.

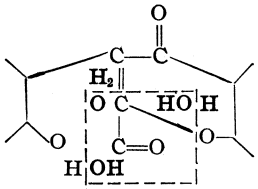


III



IV

A compound of formula III, like rotenone, might be expected to undergo alkaline hydrolysis with the formation of derritol. The experiment showed that this reaction does in fact take place. A small yield of derritol was obtained from rotenonone under the same conditions that were employed for the preparation of derritol from rotenone.[5] The main product, however, was an acid which failed to crystallize.



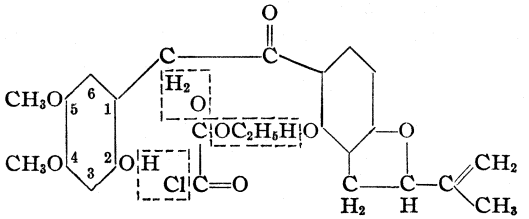
Rotenononic acid gives a positive test for phenol with ferric chloride and is easily methylated by dimethyl sulfate to the methyl ester of methylrotenononic acid, which separates in crystalline form from the alkaline solution. The corresponding acid is obtained from the ester. The ester is also easily hydrogenated to the tetrahydro derivative, which is alkali soluble.

Contrary to expectations, methyltetrahydrorotenononic acid is not cleaved by hydrogen peroxide to asaronic acid. The resistance of rotenononic acid toward strong alkali is also quite remarkable and indicates an unusual stability of the complex represented by formula IV.

[4] LaForge and Smith, THIS JOURNAL, **52**, 3603 (1930).

[5] LaForge and Smith, *ibid.*, **51**, 2574 (1929).

If formula III is a correct expression for rotenonone, it should be possible to effect the synthesis of rotenonone from derritol by substitution of the oxyalyl ethyl ester radical on the free phenol group in position 2 followed by saponification and dehydration, as in the formation of dehydrorotenone from derrisic acid. The reaction is represented below.



Derritol was therefore allowed to react with chloro-oxalyl ethyl ester in pyridine solution. It was expected that the oxalyl ethyl ester would result, which could subsequently be saponified and dehydrated to rotenonone. However, under the conditions of the experiment all three reactions took place spontaneously, and there resulted a nearly quantitative yield of rotenonone. In view of the small yield of rotenonone obtained by oxidation of rotenone, this method is probably the most convenient one for its preparation.

There can be no further doubt that rotenonone is represented by formula III.[6]

Experimental

Rotenononic Acid.[1]—Two grams of rotenonone was added to a boiling solution of 2 g. of solid potassium hydroxide in 2 cc. of water to which 6 cc. of alcohol had been added. The solution was boiled for five minutes, then diluted with water and acidified. The amorphous precipitate crystallized directly, and the product was purified by dissolving in a large quantity of hot alcohol, filtering if necessary from a small residue of rotenonone and concentrating to a small volume. The compound crystallized slowly. The yield was about 1.7 g. It melted at 250°.

Methylrotenononic Acid Methyl Ester.—Four grams of rotenononic acid dissolved in 35 cc. of 5% potassium hydroxide was methylated with 7 g. of dimethyl sulfate. The reaction was carried out with mechanical stirring over a period of two hours.

The product separated crystalline and was recrystallized from methyl alcohol. It melted at 138°. The yield was 3.5 g.

Anal. Subs., g. 0.0790, 0.0207, 0.0198: CO_2, 0.1906; H_2O, 0.0386. Thiosulfate solution (1 cc. = 0.000520 CH_3O), 10.7, 10.15. Calcd. for $C_{25}H_{24}O_8$: C, 66.37; H, 5.32; $4CH_3O$, 27.43. Found: C, 65.80; H, 5.43; CH_3O, 26.90; 26.68.

The corresponding acid was obtained by saponification of the ester. It was recrystallized from a small quantity of methyl alcohol. It melted at 179–180°.

Anal. Subs., 0.0777, 0.0272 g.: CO_2, 0.1864; H_2O, 0.0374. Thiosulfate (1 cc. =

[6] An article by Butenandt and McCartney [*Ann.*, **494**, 17 (1932)] has just reached us, April 20, as the foregoing article is being submitted for publication in which the authors have expressed the formula for rotenonone by a formula identical with III.

0.000520 CH_3O), 11.00. Calcd. for $C_{24}H_{22}O_8$: C, 65.75; H, 5.02; $3CH_3O$, 21.23. Found: C, 65.43; H, 5.34; CH_3O, 21.04.

Tetrahydromethylrotenononic Acid.—Two grams of methylrotenononic acid methyl ester was reduced with platinum catalyst in acetic ester solution until the required four atoms of hydrogen were absorbed. The solution was extracted with cold dilute alkali, and, after standing for some time to allow the ester to saponify, the aqueous solution was acidified and the product recrystallized from dilute alcohol. A small sample was recrystallized from very little methyl alcohol. The melting point was 184–186°.

Anal. Subs., 3.542, 3.149 mg.: CO_2, 8.495, 7.588; H_2O, 1.949, 1.712. Calcd. for $C_{24}H_{26}O_8$: C, 65.18; H, 5.88. Found: C, 65.42, 65.71; H, 6.11, 6.04.

Derritol from Rotenonone.—Three grams of rotenonone was boiled with zinc and alcoholic potassium hydroxide under the same conditions as for the preparation of derritol from rotenone.[5]

The solution was filtered and acidified, and the precipitate was dissolved in ether. The ether solution was extracted with aqueous carbonate solution, which removed a considerable quantity of an acid which was recovered by acidifying the solution and extracting with ether. The material remaining after evaporation of the ether represented by far the larger part of the reaction product, but it could not be made to crystallize.

The first ether solution was then extracted with dilute potassium hydroxide solution. The alkaline solution was acidified and extracted with ether. The ether solution gave on evaporation 0.06 g. of derritol. It was recrystallized and compared with an authentic sample by the mixed melting point and crystal form. It melted at 161°.

Anal. Subs., 2.989 mg.: CO_2, 7.388; H_2O, 1.654. Calcd. for $C_{21}H_{22}O_6$: C, 68.07; H, 5.99. Found: C, 67.41; H, 6.15.

Synthesis of Rotenonone from Derritol.—Two grams of derritol was dissolved in 5 cc. of pyridine. The solution was cooled in an ice-bath and 2.5 g. of chloro-oxalyl ethyl ester[7] was slowly added. The reaction mixture was allowed to stand for forty-eight hours, after which time the contents of the flask had become a semi-solid mass of fine yellow crystals. Alcohol was added and the solid material filtered off. The product was recrystallized by dissolving in chloroform and adding hot alcohol. It formed yellow needles and possessed all the characteristic properties of rotenonone. The melting point was 298°; mixed melting point 298–300°. The yield was 1.6 g. of pure material.

Anal. Subs., 0.0257, 0.0249: thiosulfate (1 cc. = 0.000520 CH_3O) 7.30, 7.05. Calcd. for $C_{23}H_{18}O_7$: $2CH_3O$, 15.27. Found: CH_3O, 14.77, 14.69.

Summary

Rotenonone is partially converted into derritol by zinc alkali hydrolysis. Rotenononic acid is methylated by dimethyl sulfate to the methyl ester of methylrotenononic acid. Methylrotenononic acid is hydrogenated to a tetrahydro compound.

Rotenonone is the lactone corresponding to rotenononic acid.

The synthesis of rotenonone from derritol was accomplished by the substitution of the oxalyl ethyl ester groups on the reactive phenolic group in pyridine solution. Complete condensation to rotenonone took place in one operation with the formation of rotenonone.

WASHINGTON, D. C.

[7] Anschütz, *Ann.*, **254**, 27 (1889).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. XI. CONSTITUENTS OF THE MILLED RUBBER HYDROCARBON

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

RECEIVED APRIL 22, 1932 PUBLISHED AUGUST 5, 1932

The tenth paper of this series[1] has shown that *unmilled* pale crepe rubber contains a single "sol" component, which constitutes more than one-half of the specimen, and a continuous series of undefined "sol" portions amounting to about 20% of the specimen. These results have been obtained by a fractional precipitation from a benzene–alcohol mixture.

The same method of investigation has now been applied to *thoroughly milled* pale crepe rubber, and the present paper shows that the whole specimen is made up of a continuous series of undefined "sol" components, in undefined proportions.

Procedure.—Pale crepe rubber was milled for one hour on cold rolls. A 250-g. specimen was dissolved in benzene, and fractioned into primary cuts, by the method described.[1] Although the principle of fractionation remained unchanged, minor experimental details were altered, as follows.

Milled rubber is much more soluble in a given benzene–alcohol mixture than unmilled rubber. To illustrate: the s. p. p.'s[1] of the rubber specimen used, before and after milling, were 35.4 and 27.7°, respectively. Consequently, in order to be able to carry out the fractionation at a convenient temperature, *viz.*, about 40°, the solvent was made richer in alcohol than previously reported. In all cases, the length of time allowed for separation was extended to fourteen hours. Chilling out was accomplished by letting the solutions stand (under vacuum) in a refrigerator at about −10° for six hours. Since the fractions obtained from milled rubber did not precipitate sharply from an alcohol–benzene mixture, the experimental precipitation point could not be duplicated closer than ±0.2°.

Table I shows the results of the primary fractionation.

TABLE I

PRIMARY FRACTIONATION OF 250 G. OF MILLED CREPE RUBBER

Fractions	Amounts, g.	Standard precipitation point (s. p. p.) in degrees	% based on 233.4 g.	
A_0	36.4	23.2	15.6	
A_1	66.4	23.4	28.4	81.2
A_2	68.5	24.3	29.3	
A_3	30.3	24.9	13.0	
A_4	24.5	24.9	10.5	
B	7.3	Not obtained	3.1	
Total	233.4		99.9	
Losses	16.6			

Fractions A_1 to B inclusive were obtained by the previously described method of operation.

[1] Midgley, Henne and Renoll, THIS JOURNAL, **54**, 3343 (1932).

Fraction A_0 was found in the supernatant liquid remaining after the separation of A_1, in the following manner: the liquid was cooled to $-10°$ and kept at that temperature until the lower half of the mixture (containing the rubber and benzene) had frozen. The upper half containing the so-called "resins" was decanted, and the rubber was precipitated from the benzene of the lower half with acetone.

The reported losses include an estimated amount of 12.5 g. of "resins," soluble in alcohol. Hence the actual losses amount only to 4 g., *viz.*, about 1.5%.

The tabulated results appear on the chart, where the percentages of rubber are plotted against the s. p. p. They are represented by the solid line. The length of the abscissa measures the size of fractions A_0 to A_4 inclusive. The s. p. p. of fraction B could not be determined, because it was insoluble. It was extracted with boiling benzene for several days, but the solvent removed only 1.1 g. of rubber. This B fraction was a nearly white, fibrous mass with a nitrogen content of 9.4%.

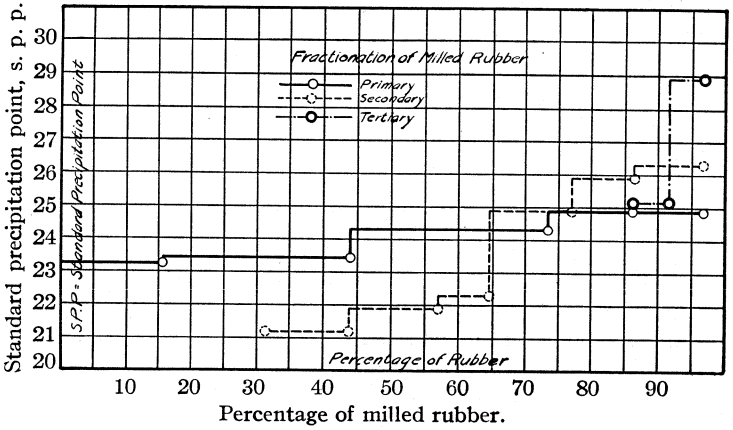


Fig. 1.—Fractionation of milled rubber.

Each of the primary cuts from A_1 to A_4, (*viz.*, 81.2% of the rubber recovered) was refractioned. A_3 and A_4 were combined because they had the

TABLE II

SECONDARY FRACTIONATION OF FRACTIONS A_1 TO A_4, *viz.*, 81.2% OF THE RUBBER RECOVERED

Fractions		Amount, g.	S. p. p. in degrees	% based on 81.2% = 189.7 g.
A_1	Top	28.6	21.2	12.2
	Bottom	27.2	24.9	11.6
A_2	Top	31.4	21.9	13.4
	Bottom	24.5	25.9	10.5
A_{3-4}	Top	17.9	22.3	7.7
	Bottom	23.7	26.3	10.2
Total recovered		153.3		65.6
Remaining in solution		36.4		15.6
Total		189.7		81.2

same s. p. p. The refractionation was carried out at 50°; the results appear in Table II, and on the diagram.

The 36.4 g. of rubber remaining in solution could have been recovered in the manner used for A_0, in the primary fractionation; but this was considered superfluous for the present research.

The tables and diagram show that there is no indication of a single component, present in large proportion.

The fraction called "A_{3-4} bottom," in Table II was then refractioned, to give the results shown in Table III.

TABLE III

TERTIARY FRACTIONATION OF A_{3-4}

Fractions		Amount, g.	S. p. p. in degrees	% based on 10.2% fractioned
A_{3-4}	Top	9.5	25.1	4.7
	Bottom	11.3	28.9	5.5
Total		20.8		10.2

The efficiency of the separation method is illustrated as follows: a 10-g. specimen (s. p. p. 35°) obtained from *unmilled* rubber and a 10-g. sample (s. p. p. 28.9°) obtained from the fraction called [A_{3-4}, bottom], in Table III, were dissolved in the same batch of benzene, and separated by fractional precipitation. A single fractionation yielded 11.5 g. of s. p. p. 34.9° and 85. g. of s. p. p. 28.5°. This experiment demonstrates that the fractionation method separates with ease individual components.

The appearance of the various cuts was as follows. The fractions with low s. p. p. were almost colorless, transparent and very tacky. The higher s p. p fractions were less tacky, and they were yellow; in spite of the color, they did not have the appearance of oxidized rubber.

Conclusion.—Fractional precipitation shows that *milled* rubber is constituted of a continuous series of undefined components. Milling degrades the components of *unmilled* rubber into materials of lower s. p. p. without producing a single predominating component.

Summary

The composition of *milled* rubber has been investigated by a method based on fractional precipitation from a benzene–alcohol mixture. This has shown that milled rubber is made of a continuous series of undefined components, without a single predominating individual. The same method had previously shown that one single individual constituted more than one-half of unmilled rubber.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

SYNTHESES WITH TRIARYLVINYLMAGNESIUM BROMIDES. PENTAARYLALLYL ALCOHOLS

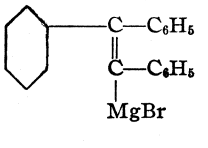
BY C. FREDERICK KOELSCH[1]

RECEIVED APRIL 27, 1932 PUBLISHED AUGUST 5, 1932

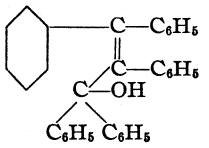
The interest attaching to compounds of trivalent carbon in which the methane carbon atom bears two aryl groups and one unsaturated aliphatic group has led to the investigation described in this paper. The object of this research has been to synthesize a pentaarylallyl radical, $R_2C{=}CR{-}CR_2{-}$, and to compare the behavior of this substance with that of the less highly phenylated tetraarylallyl radicals, $R_2C{=}CH{-}CR_2{-}$, of Ziegler. Although this object has not yet been attained, the present results are presented for their inherent interest.

It was reported previously[2] that triphenylvinylmagnesium bromide (I) reacted with benzophenone to form an addition product whose hydrolysis gave back the ketone and triphenylethylene. When, however, the reaction is carried out at an elevated temperature in toluene solution, it follows the normal course, yielding an —OMgBr compound whose hydrolysis gives pentaphenylallyl alcohol (II).

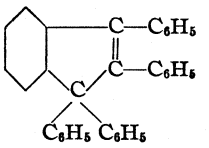
In order to prepare a radical from pentaphenylallyl alcohol it is necessary to convert it first into a halide or an ether, but no means have yet been found for carrying out either of these reactions. When this alcohol is treated with any acidic reagent, even cold 1% alcoholic sulfuric acid, it loses water, forming a hydrocarbon $C_{33}H_{24}$. Since the oxidation of this hydrocarbon gives *o*-benzoyltriphenylcarbinol (IV) and benzoic acid, and further diphenylphthalide (V), it must be 1,1,2,3-tetraphenylindene (III).



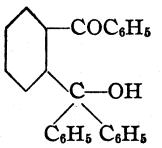
I



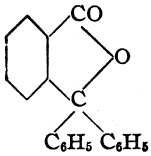
II



III



IV



V

The ease with which indene ring closure takes place in pentaphenylallyl alcohol results, at least in part, from the spatial arrangement of the atoms in the molecule. In Fig. 1 is shown a diagrammatic representation of the

[1] National Research Fellow in Chemistry.

[2] Koelsch, THIS JOURNAL, 54, 2045 (1932).

arrangement of the part of the molecule involved in the reaction. In this diagram the assumptions are made that (1) all joined carbon atoms are at an equal distance a from each other; (2) the valence of the phenyl group extends radially; and (3) the valences of the aliphatic carbon atoms are inclined to the double bond at an angle of 109°. None of these assumptions is more than approximately true, but together they allow the calculation of the distance d between the o-position of the γ-phenyl group and the hydroxyl-bearing carbon atom. This distance is found to be $1.14a$.

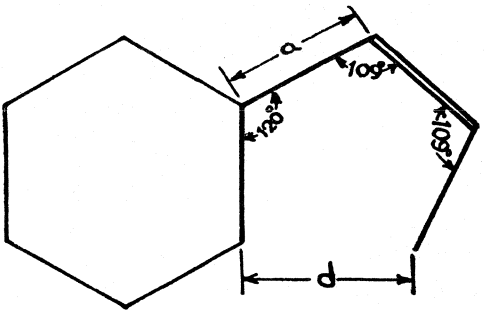


Fig. 1.—The spatial arrangement of pentaphenylallyl alcohol.

These steric considerations suggest a basis for synthesizing a pentaarylallyl alcohol unable to undergo indene ring closure. If the two phenyl groups on the γ-carbon atom are tied together, the conditions existing may be represented as in Fig. 2. Again, all joined carbon atoms are assumed to be at equal distances, and the pentagon involved in the structure is assumed to be regular. Here the distance d between the o-position of the γ-phenyl (ene) group and the hydroxyl-bearing carbon atom is calculated to be $1.86a$. Indene ring closure, since it involves the joining of these positions, should thus be impossible.

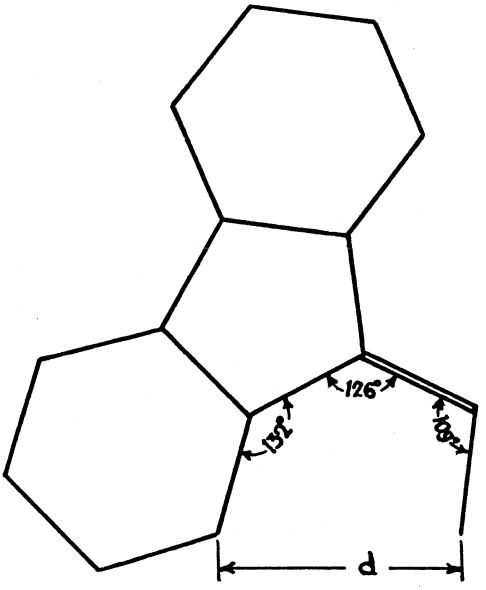
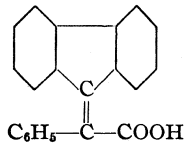


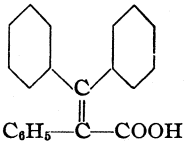
Fig. 2.—The spatial arrangement of α,α,β-triphenyl-γ-diphenyleneallyl alcohol.

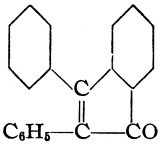
These calculations were experimentally verified using α-phenyl-β-diphenyleneacrylic acid (VI). This acid and its chloride are stable under conditions[3] which lead to the formation of diphenylindone (VIII) or substituted diphenylindones from α,β,β-triphenylacrylic acid (VII) or its derivatives.

α-Phenyl-β-diphenylenevinylmagnesium bromide (IX) reacts with benzophenone to produce the expected α,α,β-triphenyl-γ-diphenyleneallyl

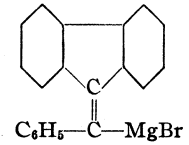
[3] Koelsch, THIS JOURNAL, 54, 2487 (1932).

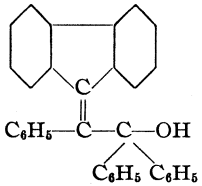

VI

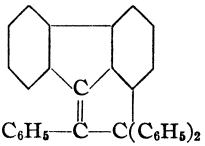

VII

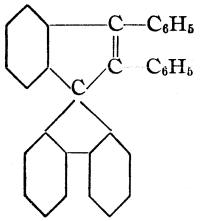

VIII

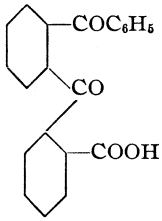
alcohol (X). Surprisingly, it was found that here, too, as in the case of pentaphenylallyl alcohol, even the mildest acidic reagents cause the elimination of water with the formation of a hydrocarbon $C_{33}H_{22}$. The oxidation of this hydrocarbon gives *o*-benzoylbenzophenone-*o*-carboxylic acid (XIII) and benzoic acid, showing that the "impossible" indene ring closure does not take place with the formation of (XI), but that an allylic rearrangement accompanies the dehydration, and that the hydrocarbon $C_{33}H_{22}$ is 1-diphenylene-2,3-diphenylindene (XII).

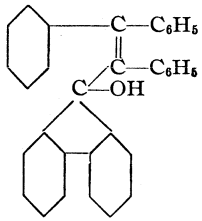

IX


X


XI


XII


XIII


XIV

Finally, α-diphenylene-β,γ,γ-triphenylallyl alcohol (XIV), obtained from triphenylvinylmagnesium bromide and fluorenone, is distinctly different from its isomer (X), but treatment with an acidic reagent causes it to lose water with the formation of the same 1-diphenylene-2,3-diphenylindene (XII).

A subsequent paper will describe α,γ-bisdiphenylene-β-phenylallyl alcohol and its conversion into a radical.

Experimental

Benzalfluorene Dibromide.—A hot solution of 85 g. of benzalfluorene in 85 ml. of acetic acid is cooled rapidly to form a fine crystalline suspension, and at 20–35° (cooling) is added a solution of 55 g. of bromine in 55 ml. of acetic acid. On scratching and further cooling the dibromide separates. It is filtered off and washed with dilute acetic acid and with water; yield, 126 g. or 91%. The product melts at 116° with decomposition (literature[4] 112°). Recrystallization is unnecessary and causes some decomposition.

[4] Thiele and Henle, *Ann.*, **347**, 298 (1906).

α-Phenyl-β-diphenylenevinyl Bromide.—This compound can be prepared by the thermal decomposition of benzalfluorene dibromide, either in acetic acid or without a solvent, but the product thus obtained in a yield of 25–30% is difficult to purify. The decomposition in acetic acid in the presence of sodium acetate is likewise very unsatisfactory.

The following method gives a yield of 85–89%. A solution of 30 g. of potassium hydroxide in 15 ml. of water and 100 ml. of alcohol is added to a solution of 125 g. of benzalfluorene dibromide in 300 ml. of alcohol. The mixture is stirred vigorously and refluxed for twenty-five minutes on a water-bath. The solid product is filtered off after cooling, washed well with water and recrystallized from acetic acid (600–625 ml.). There is obtained 86 g. of pure bromide, and from the mother liquor by distilling to 50 ml. an additional 2.5 g. The product crystallizes in yellow prisms that melt at 127°.

Anal. Calcd. for $C_{20}H_{13}Br$: C, 72.0; H, 3.9. Found: C, 71.8; H, 3.9.

α-Phenyl-β-diphenylenevinylmagnesium Bromide (IX).—The Grignard reagent is prepared according to the usual procedure[3] for triarylvinylmagnesium bromides. It separates as a green oil difficultly soluble in ether, or as yellow crystals.

Reaction with Benzoyl Chloride.—To the Grignard reagent from 5 g. of the bromide is added an ether solution of 2 ml. of benzoyl chloride. The product, α-phenyl-β-diphenyleneacrylophenone, is isolated in the usual way and crystallized from ethyl acetate. It forms small yellow plates that melt at 300–303°.

Anal. Calcd. for $C_{27}H_{18}O$: C, 90.5; H, 5.0. Found: C, 90.5; H, 5.1.

α-Phenyl-β-diphenyleneacrylic Acid (VI).—The Grignard reagent from 6.5 g. of α-phenyl-β-diphenylenevinyl bromide is carbonated in the usual way,[3] and the product is crystallized from acetic acid. It forms fine needles that melt at 182–183°. It is soluble in cold concd. sulfuric acid, giving a pale green solution that becomes colorless on dilution with water.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.5; H, 4.7; neut. equiv., 298. Found: C, 84.0; H, 4.6; neut. equiv., 298.

Reaction with Thionyl Chloride.—Equal weights (0.5 g.) of α-phenyl-β-diphenyleneacrylic acid and thionyl chloride are refluxed together in 2 ml. of carbon tetrachloride for four hours. No red color appears. The solution is stirred into cold aqueous ammonia, the carbon tetrachloride is evaporated and the remaining solid is crystallized from alcohol. The yellow product, α-phenyl-β-diphenyleneacrylamide, melts at 128–129° and gives a test for nitrogen.

Anal. Calcd. for $C_{21}H_{15}ON$: C, 84.8; H, 5.0. Found: C, 85.0; H, 5.3.

Pentaphenylallyl Alcohol (II).—To the Grignard reagent from 10 g. of triphenylvinyl bromide is added 5 g. of benzophenone. Toluene is added and the mixture is distilled to 85°. It is refluxed until the bright red color has changed to light yellow (about four hours) and then it is allowed to stand for ten hours. The crystalline magnesium compound is filtered off, washed with dry ether and decomposed with iced ammonium chloride containing some ammonia. The oil is taken up in ether. This solution is dried with potassium hydroxide, distilled to a small volume under reduced pressure and mixed with petroleum ether. The product crystallizes very slowly; yield, 3.1 g.

The combined mother liquors from this preparation give 2.25 g. of tetraphenylindene on treatment with acid.

Pentaphenylallyl alcohol forms small white crystals that melt at 108–109°; its solution in acetic acid gives a green color with acetyl chloride or sulfuric acid that disappears immediately.

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.4; H, 5.9. Found: C, 90.1; H, 6.0.

$\alpha,\alpha,\beta,\gamma,\delta,\delta$-Hexaphenylbutadiene.—This hydrocarbon (0.4 g.) was isolated from the mother liquors of a preparation of pentaphenylallyl alcohol involving 20 g. of triphenylvinyl bromide. It can be prepared from triphenylvinylmagnesium bromide and cupric chloride[5] in a 55% yield. It crystallizes from benzene and petroleum ether in faintly yellow needles that melt at 213–214°.

Anal. Calcd. for $C_{40}H_{30}$: C, 94.2; H, 5.8. Found: C, 93.9; H, 5.8.

α,α,β-Triphenyl-γ-diphenyleneallyl Alcohol (X).—To the Grignard reagent from 5 g. of α-phenyl-β-diphenylenevinyl bromide is added 2 g. of benzophenone. The mixture is refluxed for three hours and allowed to stand for twenty-four hours or until the original red-brown color has faded to a light tan. The solid magnesium compound is removed, washed with ether and decomposed with iced ammonium chloride. The crude solid is washed with alcohol containing a little ammonia, dried and crystallized from benzene and petroleum ether; yield, 1.75 g. The alcohol forms yellow prisms that melt at 217–219°; its solution in acetic acid gives no color with sulfuric acid; with hot concd. sulfuric acid the alcohol gives a green color which is permanent on dilution with water.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.9; H, 5.5. Found: C, 90.9; H, 5.6.

α-Diphenylene-β,γ,γ-triphenylallyl Alcohol (XIV).—Fluorenone (2 g.) is added to the Grignard reagent from 5 g. of triphenylvinyl bromide. The solution is treated and the product is isolated as described under α,α,β-triphenyl-γ-diphenyleneallyl alcohol. The product is crystallized from alcohol containing a little ammonia, and then from carbon tetrachloride and petroleum ether; yield, 1.35 g. α-Diphenylene-β,γ,γ-triphenylallyl alcohol forms colorless crystals that melt at 150–151°.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.9; H, 5.5. Found: C, 91.0; H, 5.5.

Dehydration of the Pentaarylallyl Alcohols.—All of the alcohols described above lose water to form colorless indenes when cold dilute alcoholic sulfuric acid is added to their solutions in methyl or ethyl alcohol. The indenes are best prepared by warming an acetic acid solution of an allyl alcohol with a few drops of sulfuric acid, hydrochloric acid, or acetyl chloride. They can also be prepared by boiling the alcohols with undiluted acetyl chloride. The data concerning the indenes recrystallized from acetic acid are summarized in Table I.

TABLE I

THE INDENES (III) AND (XII)

( )-indene	M. p., °C.	Formula	Analysis Calcd. C	Calcd. H	Found C	Found H
1,1,2,3-Tetraphenyl-	149–150	$C_{33}H_{24}$	94.2	5.8	94.0	5.8
1-Diphenylene-2,3-diphenyl-	[a]174–175	$C_{33}H_{22}$	94.7	5.3	94.5	5.3
	[b]174–175				94.5	5.3

[a] From α,α,β-triphenyl-γ-diphenyleneallyl alcohol.
[b] From α-diphenylene-β,γ,γ-triphenylallyl alcohol.

Oxidation of 1,1,2,3-Tetraphenylindene

(a) To *o*-Benzoyltriphenylcarbinol (IV).—To a solution of 1.85 g. of the hydrocarbon in acetic acid is added 5 g. of chromic acid in acetic acid and water. After refluxing for one hour the mixture is poured into water and extracted with ether. Sodium carbonate removes benzoic acid from the ether extract, and steam distillation gives 0.13 g. of benzophenone. Since the residue crystallizes with great difficultly, it is con-

[5] *Cf.* Sakellarios and Kyrimis, *Ber.*, **57**, 322 (1924).

verted into 9,9-diphenylanthrone by distillation.[6] There is obtained 0.55 g. of the crude anthrone (m. p. 180–190°) which after crystallization from toluene and ligroin melts at 191–193° alone or mixed with a known sample of diphenylanthrone.[7]

(b) **To Diphenylphthalide (V).**—The oxidation is carried out as in (a) using 1.7 g. of tetraphenylindene and 9 g. of chromic acid. From the ether extract of the oxidation products is obtained 0.1 g. of benzoic acid. The oily residue left after the removal of the ether from the neutral part becomes crystalline on rubbing with alcohol, and after recrystallization from this solvent the product, diphenylphthalide, melts at 114–115° (mixed m. p.) and weighs 0.5 g.

Oxidation of 1-Diphenylene-2,3-diphenylindene.—The hydrocarbon (3.9 g.) in acetic acid is oxidized with 12 g. of chromic acid by refluxing for two hours. The solution is poured into water and extracted with ether. Sodium carbonate removes benzoic acid and *o*-benzoylbenzophenone-*o'*-carboxylic acid; the former (0.25 g.) is dissolved out with warm water, leaving 0.6 g. of the crude keto acid. This melts at 224–225° (literature[8] 228°) and weighs 0.4 g. after recrystallization from acetic acid.

Anal. Calcd. for $C_{21}H_{14}O_4$: C, 76.3; H, 4.2. Found: C, 76.2; H, 4.3.

On treatment with ethereal diazomethane the acid gives the methyl ester, which melts at 162–163° (literature[8] 165°); on heating with sulfuric acid, it gives the lactone of 9-*o*-carboxyphenyl-9-oxyanthrone-10 which melts at 235–237° (literature[8] 239°).

The neutral substance not removed from the ether solution of the oxidation products by sodium carbonate is crystallized from acetic acid, distilled at 15 mm. and recrystallized. There is obtained 0.1 g. of a white *compound*[9] crystallizing in needles that melt at 204–206°.

Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.6; H, 4.5. Found: C, 83.4; H, 4.5.

Summary

Triphenylvinylmagnesium bromide reacts with benzophenone and with fluorenone to give pentaarylallyl alcohols. On treatment with acids these alcohols lose water forming tetraarylindenes.

α-Phenyl-β-diphenylenevinylmagnesium bromide and carbon dioxide give α-phenyl-β-diphenyleneacrylic acid, which because of its steric arrangement cannot form an indone.

α,α,β-Triphenyl-γ-diphenyleneallyl alcohol, obtained from α-phenyl-β-diphenylenevinylmagnesium bromide and benzophenone, is prevented from forming an indene by its steric arrangement. However, acids cause it to undergo an allylic rearrangement, the resulting alcohol then losing water to form a tetraarylindene.

CAMBRIDGE, MASSACHUSETTS

[6] Barnett, Cook and Nixon, *J. Chem. Soc.*, 510 (1927).

[7] Howell, THIS JOURNAL, **42**, 2335 (1920).

[8] Cook, *J. Chem. Soc.*, 62 (1928).

[9] It was thought that this compound might be diphenylenephthalide, and that it might be prepared by the oxidation of 9-*o*-tolyl-9-oxyfluorene, but it has not been possible to isolate a lactone from the oxidation products of this carbinol. 9-*o*-Tolyl-9-oxyfluorene was obtained in good yield from *o*-tolylmagnesium iodide and fluorenone. After crystallization from acetic acid it melted at 118–119° and gave a deep red color with concd. sulfuric acid.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 87.8; H, 5.9.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

HEMI-ACETALS OF ALDEHYDO-GALACTOSE PENTAACETATE AND THEIR OPTICAL PROPERTIES

BY M. L. WOLFROM AND WILLIAM M. MORGAN

RECEIVED APRIL 28, 1932 PUBLISHED AUGUST 5, 1932

The open-chain or aldehydo form of galactose pentaacetate forms a crystalline addition compound with one mole of ethyl alcohol.[1] Brigl and Muehlschlegel[2] have reported a similar compound for aldehydo-glucose pentabenzoate. In the case of the galactose compound, we have produced evidence[3] that the substance is a true hemi-acetal of unusual stability. Such a compound is thus the open-chain analog of the glycosides which are monocyclic acetals. In view of the great amount of research which has been done on the latter compounds, it was considered of interest to study the corresponding open-chain galactose compounds in somewhat more detail. Accordingly the hemi-acetals of aldehydo-galactose pentaacetate with a number of aliphatic alcohols will now be reported. That the carbonyl group in the sugar acetate used possesses the power of adding an alcohol of relatively large molecular weight is shown by the successful preparation of a compound with cyclohexanol.

The ethyl hemi-acetal showed a mutarotation curve in chloroform (alcohol-free) which passed through a minimum and was thus indicative of a three-membered equilibrium. This was explained[3] by the following equation, the carbonyl carbon atom being asymmetric in the hemi-acetal and so existing in two forms

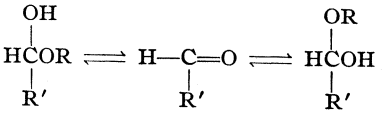


Figure 1 shows that a similar type of curve is obtained for the other hemi-acetals now prepared. It is to be noted that as the molecular weight of the alcohol increases, the dissociation in chloroform solution is more rapid, this being indicated by the steepness of the first part of the curve.

The investigation of the optical properties of these hemi-acetals has a direct bearing upon the theory of sugar mutarotation because the open-chain form of the sugar or its aldehydrol is postulated as the most probable intermediate in this reaction.[4] From the standpoint of organic structural theory, the mutarotation of an aldehydo hemi-acetal in its own alcohol is

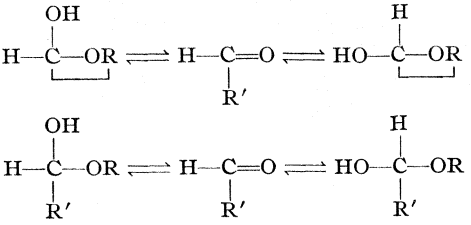
[1] Wolfrom, THIS JOURNAL, **52**, 2464 (1930).

[2] Brigl and Muehlschlegel, *Ber.*, **63**, 1551 (1930).

[3] Wolfrom, THIS JOURNAL, **53**, 2275 (1931).

[4] Lowry, "Rapports sur les Hydrates de Carbone. Dixième Conférence de l'Union International de Chimie," Liège, 1930, p. 79.

quite analogous to the mutarotation of a sugar (a cyclic hemi-acetal) in water as the following formulas show



Of the hemi-acetals prepared, only the methanol compound possessed a solubility in its corresponding alcohol suitable for polarimetric observation at room temperature. Figure 2 shows that this compound in methanol exhibits a typical sugar mutarotation curve and the data of Table I place the reaction as apparently monomolecular. In view of the low rotations and the long time involved, the slight deviation from constancy of the values obtained is within the limits of experimental error. The presence of the intermediate aldehyde in methanol solution is thus undetectable by polarimetric measurement, while in chloroform solution an intermediate form is easily detectable. It appears reasonable that the intermediate is the same in both cases but that the concentration of the intermediate form is much greater in the chloroform solution.

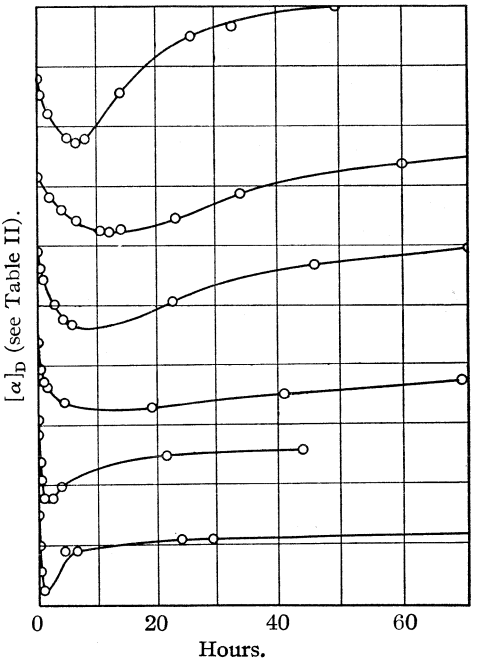


Fig. 1.—Mutarotation of several hemi-acetals of aldehydo-galactose pentaacetate in chloroform (alcohol-free). Order, from top to bottom: methyl, ethyl, *n*-propyl, isopropyl, isobutyl, cyclohexanol.

In the course of this work it was necessary to prepare considerable quantities of aldehydo-galactose pentaacetate and a somewhat simplified method of preparation for this substance was devised.

Experimental

Preparation of Aldehydo-galactose Pentaacetate.—The mercaptal groups were removed from galactose ethyl mercaptal with mercuric chloride in acetone solution to which had been added only 25 cc. of water for 50 g. of the acetylated mercaptal, the proportions of the other reagents being the same as previously reported.[1] The evapo-

TABLE I

MUTAROTATION OF THE METHYL HEMI-ACETAL OF ALDEHYDO-GALACTOSE PENTAACETATE IN METHANOL

l, 4-dm.; λ 5892 Å.; *t*, 24°; *c*, 2.006

t, min.	α, degrees	$[\alpha]_D$, degrees	*k*
0	..	0.0[a]	
60	+0.05	+ 0.6	6.6×10^{-4}
120	.09	1.1	6.2
255	.18	2.3	6.4
375	.25	3.1	6.0
450	.30	3.8	6.3
570	.34	4.3	5.8
735	.41	5.1	5.5
1320	.65	8.1	5.7
2190	.84	10.5	5.2
2940	.99	12.4	5.6
73 hrs.	1.09	13.6	
121	1.23	15.4	
173	1.22	15.3	

[a] Interpolated.

$$k = 1/t \ln_e \frac{\alpha_0 - \alpha_\infty}{\alpha t - \alpha_\infty}$$ [5] $\alpha_0 = 0$; $\alpha_\infty = 15.4$; t in minutes.

rated reaction mixture was dried by repeated additions of acetone followed by evaporation under reduced pressure. The residue was extracted with hot carbon tetrachloride, filtered hot and allowed to cool for the first crop of crystals. A second crop was obtained by evaporation of the mother liquor under reduced pressure. This crude product was

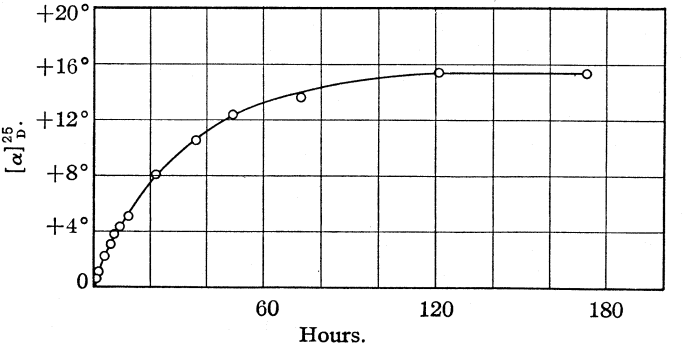


Fig. 2.—Mutarotation of the methyl hemi-acetal of aldehydo-galactose pentaacetate in methanol solution.

recrystallized by dissolving in a small amount of boiling acetone (carboraffin) cooled to room temperature and half the volume of alcohol-free ether added. Petroleum ether was then added until crystallization was initiated, an excess being avoided. After three crystallizations a yield of 11 g. of pure product (m. p. 120–121°) was obtained from 50 g. of the acetylated mercaptal. A much higher yield of slightly less pure product was

[5] Hudson, THIS JOURNAL, **26**, 1065 (1904).

readily obtainable, such material being satisfactory for the further synthetic experiments reported below.

Hemi-acetal Synthesis.—The hemi-acetals were prepared by recrystallization to constant melting point of aldehydo-galactose pentaacetate from the purified, anhydrous alcohols. For removal of the mother liquor, the filtered crystals were washed first with the cold alcohol and then with cold ether, the substances being insoluble in the latter solvent. In the case of the methyl hemi-acetal, the ether washing was omitted. A special procedure was required for the preparation of the cyclohexanol hemi-acetal. The aldehydo-galactose pentaacetate was dissolved in the least amount of cyclohexanol by warming to 80°. The solution was then quickly chilled by immersing the flask in ice water and was then treated with twice its volume of an equal mixture of absolute ethyl ether and petroleum ether. This procedure effected a good crystallization of the cyclohexanol compound. The filtered product was washed with a cold equal mixture of absolute ether and petroleum ether. The hemi-acetals prepared are shown in Table II, the ethyl compound having been reported previously. The mutarotation of the substances in alcohol-free chloroform is shown in Fig. 1.

TABLE II

HEMI-ACETALS OF ALDEHYDO-GALACTOSE PENTAACETATE, PROPERTIES AND ANALYSES

Hemi-acetal	M. p., °C.	$[\alpha]_D^{25}$ $CHCl_3$ (alcohol-free) Initial	Minimum	Final	Acetyl value (cc. 0.1 *N* NaOH per 100 mg. subs.) Calcd.	Found
Methyl	123	+3.0	− 7.7	+15°	11.8	11.7
Ethyl	133	+1.5	− 7.5	+ 6	11.4	11.4
n-Propyl	130	+4.2	− 8.2	+ 4.5	11.1	11.1
Isopropyl	144	−1	−12	− 7	11.1	10.9
Isobutyl	123	+6	− 7	+ 1	10.8	10.7
Cyclohexanol	136	0	−12	− 3	10.2	10.4

The calculated acetyl value for aldehydo-galactose pentaacetate is 12.8 cc. of 0.1 *N* sodium hydroxide per 100 mg. A methoxyl (Zeisel) determination on the methyl hemi-acetal gave the following result: Subs., 0.3019: AgI, 0.1613. Calcd. for $C_{16}H_{23}O_{11}(OCH_3)$: OCH_3, 7.35. Found: OCH_3, 7.06.

Summary

1. The following hemi-acetals of aldehydo-galactose pentaacetate have been synthesized in crystalline condition: methyl, *n*-propyl, isopropyl, isobutyl, cyclohexanol.

2. The optical properties of these compounds have been investigated and it has been shown that their behavior supports the open chain intermediate theory of sugar mutarotation.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

RESEARCHES ON THIAZOLES. XVIII. THE SYNTHESIS OF 2-PHENYLBENZOTHIAZOLE-5-CARBOXYLIC ACID AND DERIVATIVES

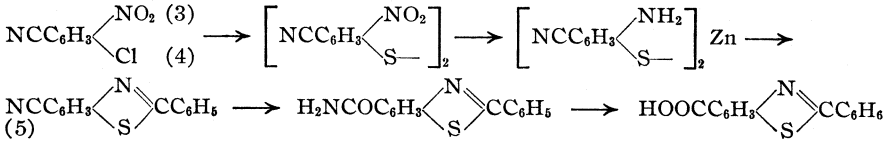
BY MARSTON TAYLOR BOGERT AND HELEN G. HUSTED[1]

RECEIVED APRIL 29, 1932 PUBLISHED AUGUST 5, 1932

In the course of certain pharmacological experiments in the benzothiazole field with which we have been occupied lately, we had occasion to prepare some of the well-known benzothiazoles by new methods and some new compounds by old methods. For the benefit of other workers in this field, these experimental results are here recorded.

In place of the processes heretofore used, we found it most convenient to prepare *o*-aminophenyl mercaptan hydrochloride, $HSC_6H_4NH_2HCl$, by treating the zinc mercaptide with concentrated hydrochloric acid, and the 2-anilinobenzothiazole, $C_6H_4\langle{}^{S}_{N}\rangle CNHC_6H_5$, from the *o*-aminophenyl disulfide and phenyl isothiocyanate.

From 3-nitro-4-chlorobenzonitrile, a series of new compounds was synthesized by the following steps



From the 2-phenyl-5-cyanobenzothiazole, a mononitro derivative was obtained, but the location of the nitro group was not determined. The methyl ester was prepared from the 2-phenylbenzothiazole-5-carboxylic acid. Both the acid and its methyl ester were too difficultly soluble to be used in our pharmacological experiments.

Experimental

From *o*-nitrochlorobenzene, there were prepared, as described in the literature and with similar results, ***o*-nitrophenyl disulfide,**[2] **zinc *o*-aminophenyl mercaptide**[3] **and *o*-aminophenyl disulfide.**[3]

***o*-Aminophenyl mercaptan hydrochloride** was obtained most conveniently by treating the zinc mercaptide (8.5 g.) with concentrated hydrochloric acid (sp. gr. 1.2) (75 cc.). The zinc salt dissolved with evolution of heat and of a trace of hydrogen sulfide. The warm solution was filtered through asbestos and the filtrate cooled in an ice pack. The hydrochloric acid salt separated rapidly in colorless needles, which were crystallized from concentrated hydrochloric acid, the crystals washed with ether, recrystallized from

[1] Ferguson Fellow, Columbia University, 1928–1929.

[2] (a) Blanksma, *Rec. trav. chim.*, **20**, 121 (1901); (b) Wohlfahrt, *J. prakt. Chem.*, [2] **66**, 555 (1902); (c) Bogert and Stull, THIS JOURNAL, **47**, 3080 (1925).

[3] Bogert and Snell, *ibid.*, **46**, 1309 (1924).

water, and then melted with decomposition at 217° (corr.) in agreement with the literature;[2c,4] yield, 80.3%.

3-Nitro-4-chlorobenzonitrile was obtained, by nitration of *p*-chlorobenzonitrile, in a yield of 61% by the Mattaar[5] method, m. p. 100–101° (corr.). Mattaar recorded the m. p. as 99–100°. It formed odorless, colorless, lustrous spangles or fine needles, readily soluble in alcohol or toluene.

Anal. Calcd. for $C_7H_3O_2N_2Cl$: C, 46.03; H, 1.64; N, 15.34. Found: C, 46.60; H, 1.63; N, 15.17.

2-Nitro-4-cyanophenyl disulfide was prepared from 3-nitro-4-chlorobenzonitrile and sodium disulfide in essentially the same way as the *o*-nitrophenyl disulfide,[2] except that refluxing of the solution was not necessary, as the disulfide separated almost immediately in fine canary yellow needles or granules, which were thoroughly washed with boiling water and then with hot alcohol; yield, 86%. When heated, these crystals began to char around 235°, and liquefied at about 335°.

Anal. Calcd. for $C_{14}H_6O_4N_4S_2$: C, 46.65; H, 1.67; N, 15.64. Found: C, 46.92; H, 1.68; N, 15.56.

2-Amino-4-cyanophenyl Mercaptan (3-Amino-4-mercaptobenzonitrile).—The zinc salt was obtained by reduction of the corresponding nitro disulfide, as described by Bogert and Snell[3] for *o*-aminophenyl mercaptan. Owing to the very slight solubility of the disulfide in hot glacial acetic acid, the reduction was carried out by intimately mixing (in a mortar) the finely pulverized disulfide with a very pure zinc dust (the purity of the zinc dust influenced the yield markedly), adding this mixture to the acid and refluxing for an hour. The product was pulverulent and pale cream colored; yield, 49%. When heated, it began to decompose at about 250°.

Anal. Calcd. for $C_{14}H_{10}N_4S_2Zn$: C, 46.28; H, 2.75. Found: C, 46.48; H, 3.39.

Benzothiazole.—*o*-Aminophenyl mercaptan hydrochloride was condensed with formaldehyde, as recorded by Claasz[6] and by Bogert and Stull.[2c]

Considerable difficulty was encountered in purifying the crude thiazole satisfactorily by distillation. At atmospheric pressure, there was much decomposition, so that the distillation had to be conducted under reduced pressure, and then the maintenance of a fairly constant pressure proved troublesome even when all connections were carefully sealed.

The fraction (A) collected at 97–100° at 18.6 mm. was used for some of the pharmacological experiments which will appear shortly in the *J. Pharmacol. and Exptl. Therapeutics*, and when tested by the Siwoloboff[7] method showed a b. p. of 231° (corr.) at atmospheric pressure, in accordance with the figure given by Hofmann[4a] and by Bogert and Stull.[2c] From another run, the fraction (C) boiling at 87–91° at 11 mm., 231° (corr.) at 760 mm. was used for pharmacological tests, some carried out by ourselves, and some by Professor S. W. Clausen, of the University of Rochester, in connection with his studies on experimental eczema.

The carefully purified material (b. p. 231°, corr.) showed the following constants: $n_D^{24.6}$ 1.6370; d^{22} 1.23.

Methiodide.—Fine colorless needles, melting with decomposition at 210° (corr.), in agreement with the literature.[4a]

Anal. Calcd. for C_8H_8NSI: N, 5.06. Found: N, 5.08.

---

[4] (a) Hofmann, *Ber.*, **20**, 2251 (1887).

[5] Mattaar, *Rec. trav. chim.*, **41**, 24 (1922).

[6] Claasz, *Ber.*, **49**, 1141 (1916).

[7] Siwoloboff, *ibid.*, **19**, 795 (1886).

Nitrate.—Prepared as described by Mills,[8] formed colorless crystals, but the aqueous solution of these crystals was too acidic to be suitable for our pharmacological experiments.

2-Anilinobenzothiazole, $C_6H_4\langle{}^{S}_{N}\rangle CNHC_6H_5$.—A mixture of 0.01 mole of *o*-aminophenyl disulfide and 0.02 mole of phenyl isothiocyanate was heated for forty minutes at 100°, with or without 95% alcohol as solvent. A small amount of precipitate separated and some hydrogen sulfide was evolved. Evaporation of the alcohol and crystallization of the residue from toluene gave fine colorless needles; yield, 30%; m. p., 159.2° (corr.), as compared with the figure 159° recorded by Hofmann,[9] and by Jacobson and Frankenbacher,[10] who prepared it by other methods.

Anal. Calcd. for $C_{13}H_{10}N_2S$: C, 69.03; H, 4.43. Found: C, 68.88; H, 4.71.

2-Phenyl-5-cyanobenzothiazole.—When prepared by the Bogert and Snell[3] method from the zinc aminocyanophenyl mercaptide (7.5 g.) and benzoyl chloride (12 cc.), crystallized from toluene in odorless silvery spangles, light and bulky, which melted at 197° (corr.). The yield was only 20%, as there was considerable loss in recrystallization.

Following the process of Bogert and Stull,[2c] and using benzaldehyde (2 cc.) instead of benzoyl chloride upon the zinc mercaptide (2.55 g.), the yield of thiazole was 30% and its m. p. 196.6–197.7° (corr.).

Anal. Calcd. for $C_{14}H_8N_2S$: C, 71.18; H, 3.39; N, 11.86; S, 13.59. Found: C, 71.16; H, 3.52; N, 11.76; S, 13.42.

2-Phenylbenzothiazole-5-carbamide, $H_2NCOC_6H_3\langle{}^{S}_{N}\rangle CC_6H_5$.—When the above nitrile (3 g.) was suspended in 75% sulfuric acid (80 cc.), the mixture heated for about forty-five minutes at 80°, then cooled and the brown solution poured into 900 cc. of ice water, a copious white precipitate separated which was decolorized and crystallized repeatedly from 95% alcohol. There were thus obtained colorless small needles, m. p. 247.2° (corr.), insoluble in *N* sodium hydroxide solution; yield, 23%.

Anal. Calcd. for $C_{14}H_{10}ON_2S$: N, 11.02; S, 12.59. Found: N, 10.91; S, 12.15.

Nitro-2-phenyl-5-cyanobenzothiazole.—2-Phenyl-5-cyanobenzothiazole (0.5 g.) was warmed for eighteen hours at 25° with fuming nitric acid (20 cc. of sp. gr. 1.6), and the cooled solution then poured slowly upon cracked ice. The curdy pale yellow precipitate was purified by dissolving it in a large volume of boiling 95% alcohol and adding water to incipient turbidity. The product was a colorless pulverulent solid, m. p. 256° (corr.); yield, 10%.

Anal. Calcd. for $C_{14}H_7O_2N_3S$: C, 59.78; H, 2.49. Found: C, 59.66; H, 2.71.

Not enough of this derivative was obtained to enable us to ascertain the location of the nitro group.

2-Phenylbenzothiazole-5-carboxylic Acid.—When 2-phenyl-5-cyanobenzothiazole (0.51 g.) was heated at 80° for fifteen minutes with sulfuric acid (10 cc. of a mixture of three parts by weight of concentrated acid to one of water) and then for fifteen minutes at 205°, the nitrile was saponified and on dilution with ice the thiazole acid separated. It crystallized from 95% alcohol as an odorless, colorless microcrystalline powder, and from ether in minute colorless silky needles which began to decompose around 250° and melted at about 273° (corr.); yield, 80%.

---

[8] Mills, *J. Chem. Soc.*, **121**, 460 (1922).

[9] Hofmann, *Ber.*, **13**, 12 (1880).

[10] Jacobson and Frankenbacher, *ibid.*, **24**, 1410 (1891).

Anal. Calcd. for $C_{14}H_9O_2NS$: C, 65.88; H, 3.53; N, 5.49. Found: C, 65.76; H, 3.60; N, 5.55.

It was practically insoluble in water and only slightly soluble in hot alcohol, but dissolved readily in ether or in caustic alkali solutions.

The same product was obtained by digesting 0.29 g. of the corresponding amide with 10 cc. of hydrochloric acid (sp. gr. 1.19) for a few minutes. The acid separated in crystalline form. It was removed, washed thoroughly with water, dissolved in aqueous sodium hydroxide solution, reprecipitated by sulfuric acid, this solution and reprecipitation being repeated several times and the purified acid then decolorized and crystallized from 95% alcohol, and finally from absolute alcohol; yield, 80%. The carboxyl content was determined by a Pregl micro-titration with $N/100$ sodium hydroxide solution.

Anal. Calcd. for $C_{13}H_8NSCOOH$: COOH, 17.6. Found: COOH, 18.0

Methyl Ester.—The silver salt was prepared by treating the sodium salt with silver acetate in aqueous solution. The solution was made faintly acid with nitric acid, the silver salt filtered out, washed with water, then with alcohol, dried, suspended in a methyl alcohol solution of methyl iodide, the mixture refluxed for ten minutes, diluted with methyl alcohol, the silver iodide filtered out of the hot solution, the filtrate concentrated and cooled. The methyl ester which separated was purified by recrystallization from methyl alcohol. The crystals were colorless and finely granular, m. p. 171–172° (corr.), with some previous sintering; yield, 5%.

Anal. Calcd. for $C_{15}H_{11}O_2NS$: N, 5.20. Found: N, 5.38.

Attempts to prepare the ester directly from the nitrile by the action of hydrochloric acid and methyl alcohol were unsuccessful, the original nitrile being recovered unaltered.

Summary

1. 2-Phenyl-5-cyanobenzothiazole has been synthesized from *p*-chlorobenzonitrile, by nitration of the latter, reduction of the nitrochloro compound, through the disulfide, to the 3-amino-4-mercaptobenzonitrile and the condensation of the zinc salt of the latter with either benzoyl chloride or benzaldehyde.

2. This cyanobenzothiazole has been hydrolyzed to the corresponding amide and acid, and some derivatives prepared from the latter.

3. The work was incidental to pharmacological studies which will appear elsewhere.

NEW YORK, N. Y.

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

REARRANGEMENT AND HYDROGENATION OF CERTAIN METAL ALKYLS

BY WALTER H. ZARTMAN AND HOMER ADKINS

RECEIVED APRIL 29, 1932 PUBLISHED AUGUST 5, 1932

During the course of the study of another problem, catalytically active nickel was found to exert a profound influence upon the decomposition under hydrogen of tetra alkyl and aryl lead compounds. For example, diphenyl was formed almost quantitatively (reaction 1) when tetraphenyllead was heated at 200° with a nickel catalyst for six hours under a pressure of 100 atmospheres of hydrogen. The reaction proceeded so smoothly that the product obtained directly from the reaction had practically the same melting point as purest diphenyl. Both a catalyst and hydrogen are essential for the

$$(C_6H_5)_4Pb \longrightarrow 2C_6H_5—C_6H_5 + Pb \qquad (1)$$

rearrangement indicated above, since tetraphenyllead was quite stable under 100 atmospheres of nitrogen or hydrogen at 200°, or under 100 atmospheres of nitrogen and in the presence of nickel.[1]

Tetra-*p*-tolyllead underwent a similar transformation and was converted almost quantitatively into 4,4′-dimethyldiphenyl. The reaction is not limited to tetraaryllead compounds but is also manifested by tetra-*n*-heptyllead. However, in this case the conversion was not as high, for a yield of only 62% of the theoretical amount of *n*-tetradecane was obtained. (The real yield was probably higher as mechanical losses were relatively large in this experiment.) A small amount (6%) of heptene, as determined by a bromine titration of the solvent methylcycloheptane, and presumably some *n*-heptane were produced. There was no evidence of any product boiling higher than tetradecane.

The behavior of the tetra alkyl and aryl lead compounds in the presence of catalytically active nickel is in marked contrast to that of similar compounds observed by Ipatiev, Razuvaev and Bogdanov,[1] who studied the action of hydrogen in the absence of a catalyst. These investigators found that tetramethyl-, tetraethyl- and tetraphenyllead were converted into lead and the hydrocarbon corresponding to the alkyl group as indicated in equation 2.

$$R_4Pb + 2H_2 = 4RH + Pb \qquad (2)$$

[1] The data presented in Table I would indicate that tetraphenyllead, for example, is stable at somewhat higher temperatures than would be concluded from the results obtained by Ipatiev, Razuvaev and Bogdanov [*Ber.*, **63B**, 335 (1930), and preceding papers in the *J. Russ. Phys.-Chem. Soc.*]. However, the discrepancy may well be due to the fact that we used a copper and not a glass reaction vessel, and to other differences in equipment, temperature control and purity of materials.

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS[p]

Substance	Millimoles	Time, min.	Temp., °C.	125 atm. of	Catalyst, g.	Solvent, ml.	Products	Constants
Tetraphenyllead[a]	33	360	200	H_2	4(Ni)[n]	100[g]	Diphenyl	M. p. 69–70°
Tetraphenyllead	1.95	390	200	H_2	None	25[g]	Tetraphenyllead	M. p. 227–227.5°
Tetraphenyllead	1.95	330	200	N_2	1(Ni)	25[g]	Tetraphenyllead	M. p. 224–226°
Tetraphenyllead	1.95	450	200	N_2	None	25[g]	Tetraphenyllead	M. p. 225–226°
Tetra-*p*-tolyllead[b]	26	360	200	H_2	4(Ni)	100[g]	4,4′-Dimethyldiphenyl[i]	M. p. 120–121°
Tetra-*n*-heptyllead	25	360	200	H_2	4(Ni)	100[g]	*n*-Tetradecane, 62%[j] *n*-Heptane[k] *n*-Heptene, 6%[k]	B. p. 245–9° (736 mm.)
Di-*n*-butyl zinc[c]	187	120	200	H_2	4(Ni)	None	Butane, octane, 4%	B. p. 120–125°
Di-*n*-butyl zinc	257	960	160	H_2	4(Ni)	None	Butane, octane, 3%	B. p. 120–125°
Di-*n*-butyl zinc	140	540	160	H_2	2(Ni)	75[h]	Butane, octane, 3%	B. p. 120–125°
Di-*n*-butyl zinc	112	630	160	H_2	2(Cu–Cr)[o]	75[h]	Butane	
Di-*n*-butyl zinc	128	600	130	H_2	2(Ni)	75[h]	Di-*n*-butyl zinc	
Di-*n*-butyl zinc	165	510	160	N_2	2(Ni)	75[h]	Di-*n*-butyl zinc	
Diphenylmagnesium[d]	119	480	200	H_2	4(Ni)	100[l]	Benzene, 94%[q] Diphenylmagnesium, 6%[m]	
Triphenylstibene[e]	71	450	200	H_2	4(Ni)	100[g]	Triphenylstibene	M. p. 56°

[a] M. p. 225–226°. Gilman and Robinson, THIS JOURNAL, **49**, 2315 (1927). [b] M. p. 239–240°. The method was analogous to that used for preparation of tetraphenyllead, except that *p*-bromotoluene was used in place of bromobenzene and toluene in place of benzene. [c] B. p. 70–72° (8 mm.). Noller, THIS JOURNAL, **51**, 594 (1929). [d] Noller, *ibid.*, **53**, 635 (1931). The analysis for the amount of $(C_6H_5)_2Mg$ in solution was made by means of titration with standard acid. [e] M. p. 56°. "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 80. [f] Unless otherwise noted the reaction proceeded almost quantitatively. [g] Methylcyclohexane. [h] Absolute ethyl ether. [i] M. p. 121°. Zincke, *Ber.*, **4**, 396 (1871). [j] B. p. 252° (760 mm.). Krafft, *ibid.*, **15**, 1700 (1882). [k] Heptane and heptene have approximately the same boiling points as the solvent, so that the amount of heptane could not be determined, while the heptene was determined by titration of the methylcyclohexane solution with bromine. [l] Ether containing 15 to 20% dioxane. [m] Amount determined by titration with standard acid. [n] Adkins and Covert, *J. Phys. Chem.*, **35**, 1684 (1931). [o] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931). [p] Experimental methods and apparatus were essentially the same as previously reported. Adkins and Cramer, *ibid.*, **52**, 4349 (1930). [q] The hydrogen absorption in each of two hydrogenations was approximately 400 millimoles and no cyclohexane was formed. This indicates that a compound of magnesium and hydrogen was formed. This magnesium compound was exceedingly reactive with air and water.

However, in the present work it was found that di-*n*-butyl zinc in the presence of nickel and hydrogen reacted almost entirely in the sense of equation 2, *i. e.*, zinc and butane were formed. There was only a 3 or 4% yield of octane. Di-*n*-butyl zinc reacted at a somewhat lower temperature than did tetraheptyl lead. It was stable at 130° in the presence of nickel and hydrogen but reacted rapidly at 160°.

Diphenylmagnesium behaved similarly to dibutyl zinc, that is, it was converted into benzene and what was apparently magnesium hydride. Triphenylstibene, on the contrary, was recovered unchanged after it had been subjected to the action of hydrogen and active nickel for seven and one-half hours at 200°.

It seems worth noting that the order of increasing stability of the metallic alkyls toward hydrogen in the presence of catalytically active nickel, appears to be magnesium, zinc, lead and antimony, which is the order of decreasing metallic character. With regard to the mechanism of the reaction attention should be called to the observations of Paneth and co-workers,[2] who believe that they have demonstrated that tetraethyllead decomposes into lead and ethyl radicals. The formation of diphenyl from tetraphenyllead and of benzene from diphenylmagnesium could be explained as involving in the one case the addition of two phenyl radicals and in the second case of a phenyl radical and a hydrogen atom. However, there is no apparent reason why a difference in the metal from which the phenyl radical has separated should determine the subsequent manner of combination of the radicals. There seems no justification for going beyond the conception that hydrogen and metal alkyl were in combination with the metal surface and there suffered rearrangement. A summary of the experimental results is given in Table I.

The authors are indebted to Dr. George Calingaert of the Ethyl Gasoline Corporation for the tetraheptyllead used in this investigation. Dr. Calingaert in a private communication has informed the authors that several years ago he obtained a 40% yield of *n*-butane (accompanied by ethylene and ethane) as the result of passing tetraethyllead over heated pumice. Taylor and Jones reported that when tetraethyllead is decomposed at 250–300° in the presence of hydrogen and ethylene there were produced unsaturated gaseous and liquid hydrocarbons.[3]

Summary

Nickel catalyzes a synthetic reaction whereby tetraphenyllead is converted quantitatively into diphenyl. A similar reaction occurs with tetra-*p*-tolyl- and tetraheptyllead and to a very limited extent with dibutyl

[2] Paneth and Hofeditz, *Ber.*, **62B**, 1335 (1929); Paneth and Lautsch, *ibid.*, **64B**, 2702 (1931).

[3] Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

zinc. This type of reaction represents a novel characteristic of this well-known catalyst. Nickel also catalyzes the cleavage of dibutyl zinc and diphenylmagnesium with the formation of butane and benzene, respectively.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME ANALYTICAL REACTIONS OF ALKYL SULFIDES IN BENZENE AND PURIFIED NAPHTHA SOLUTIONS[1]

JOHN R. SAMPEY,[2] KENNETH H. SLAGLE[2] AND E. EMMET REID[3]

RECEIVED APRIL 29, 1932 PUBLISHED AUGUST 5, 1932

In a study of possible agents for the removal of alkyl sulfides from hydrocarbons either by adsorption or by a chemical reaction an analytical method for the determination of sulfides, either alone or mixed with other sulfur compounds,[4] was required. Reliability and rapidity were of more importance than extreme accuracy. As the most of our work on sulfur compounds has been done, for the sake of reproducibility, in benzene this hydrocarbon was used as the solvent in this investigation. The method devised has been found to be applicable to solutions in a naphtha such as purified "Skellysolve" but, unfortunately, cannot be used when unsaturates are present.

Alkyl sulfides have usually been estimated by precipitation with mercury salts. Mabery and Smith[5] separated sulfides from Ohio petroleum by agitation of the naphtha with aqueous or alcoholic mercuric chloride. Thierry[6] used the same method to identify several sulfides from Persian oil. Faragher, Morrell and Monroe[7] recommend "normal" mercurous nitrate, $HgNO_3 \cdot H_2O$, to precipitate sulfides quantitatively from naphtha solutions.

[1] Presented in part before the Petroleum Division at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931 under the title, The Analysis of Mixtures of Sulfides, Disulfides and Mercaptans. This paper contains results obtained in an investigation of "Reactions of a Number of Selected Sulfur Compounds" listed as Project 28 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Fellow.

[3] Director, Project 28.

[4] The limitations of the method in the presence of mercaptans and disulfides will be presented in a later communication on the estimation of mixtures of mercaptans, sulfides and disulfides in benzene solution.

[5] Mabery and Smith, *Am. Chem. J.*, **13**, 233 (1891).

[6] Thierry, *J. Chem. Soc.*, **127**, 2756 (1925).

[7] Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, **19**, 1281 (1927).

More recently Faragher, Morrell and Comay[8] have made a comprehensive investigation of the interaction of alkyl sulfides and salts of mercury.

While the mercury salt method has been applied successfully to petroleum distillates, it is not applicable to the estimation of alkyl sulfides dissolved in benzene, for the complexes formed by the action of various mercury salts on the sulfides are too soluble in this solvent to give quantitative separations.

In a search for a method of analysis which might apply to benzene solutions, the action of bromine on sulfides gave some promise. G. Patein[9] observed that the bromine addition product of methyl sulfide hydrolyzed readily according to the equation $(CH_3)_2SBr_2 + H_2O = (CH_3)_2SO + 2HBr$. He determined that the hydrolysis went to completion by titration of the hydrobromic acid with caustic potash solution. It remained to be shown that the bromine addition product could be formed quantitatively from sulfides dissolved in a hydrocarbon solvent.

Method of Analysis

The procedure adopted for the analysis of alkyl sulfides in low concentration in benzene as the solvent is as follows.

A saturated solution of bromine water is added drop by drop to a mixture of 50 cc. of distilled water and exactly 50 cc. of a benzene solution of the alkyl sulfide in a 250-cc. glass-stoppered Erlenmeyer flask. The flask is shaken during the bromine treatment, and the addition is continued slowly until the color of bromine persists in the solution. Not more than two drops excess of the bromine water should be added, and this should not be permitted to remain longer than one-fourth of a minute before it is removed by the addition of a slight excess of a saturated solution of potassium iodide. The liberated iodine is then reduced with a saturated sodium thiosulfate solution. The aqueous layer is separated from the benzene layer, and the hydrobromic acid in the latter is extracted three times with 20-cc. portions of distilled water; these extracts are added to the original solution, and the hydrobromic acid content is determined by titration with $n/20$ sodium hydroxide solution, using brom cresol purple or a purified litmus solution as indicator.

Attention is invited to two precautions and one correction factor to be applied to the method. The excess bromine must be removed completely by the potassium iodide solution, for otherwise the bromine water will attack the thiosulfate solution and cause the formation of two strong acids according to the equation[10]

$$Na_2S_2O_3 + 4Br_2 + 5H_2O = H_2SO_4 + 8HBr + Na_2SO_4$$

The second precaution is similar. The iodine liberated from the potassium iodide must be removed completely by the thiosulfate solution to prevent it from acting upon the sodium hydroxide. The Erlenmeyer flask must be shaken vigorously, therefore, after the addition of the excess potassium iodide solution, and again after the introduction of the thiosulfate solution.

The correction factor which must be applied arises from the acid present in the bromine water. The exact amount of bromine water used during the oxidation must be

[8] Faragher, Morrell and Comay, THIS JOURNAL, **51**, 2774 (1929).

[9] Patein, *Bull. soc. chim.*, [2] **50**, 203 (1888).

[10] Mellor, "Inorganic Chemistry," Vol. II.

noted, and its acid content determined by shaking a like amount, dissolved in 50 cc. of water and 50 cc. of benzene, with excess potassium iodide and thiosulfate solutions, and titrating the acid. The figure thus obtained must be subtracted from the total number of cubic centimeters of alkali used in the estimation of the sulfide.

Results of Analyses

The results of the analyses with several different alkyl sulfides, and with varying concentrations of *n*-butyl sulfide, are given in Tables I and II. The solutions in Table I were prepared by weighing out in a stoppered weighing bottle the calculated amount of sulfide to give a liter of solution of 0.0500% sulfur by weight; 50-cc. portions of these solutions were pipetted for the bromine water treatment into 250-cc. glass-stoppered flasks. The samples of alkyl sulfides were supplied by Dr. L. M. Ellis, Jr.

TABLE I

ACTION OF BROMINE WATER ON ALKYL SULFIDES

Sulfide	S present, %	S found, %	Error, %
Ethyl	0.0500	0.0498	−0.4
	.0500	.0499	−0.2
Isopropyl	.0500	.0504	+0.8
	.0500	.0503	+0.6
n-Propyl	.0500	.0495	−1.0
	.0500	.0495	−1.0
Isobutyl	.0500	.0496	−0.8
	.0500	.0496	−0.8
n-Butyl	.0500	.0497	−0.6
	.0500	.0496	−0.8

The first three solutions in Table II were prepared by making up weighed quantities of the sulfide to one liter. The fourth solution (0.0045% S) was made by pipetting 5 cc. of the 0.0500% S solution into 50 cc. of benzene.

TABLE II

CHANGE IN CONCENTRATION OF *n*-BUTYL SULFIDE

S present, %	S found, %	Error, %	S present, %	S found, %	Error, %
0.2000	0.2002	+0.1	0.0500	0.0497	−0.6
.2000	.2004	+0.2	.0500	.0496	−0.8
.1000	.1002	+0.2	.0045	.0045	0.0
.1000	.1000	0.0	.0045	.0046	+2.2

Application to a Naphtha Solution Free from Unsaturated Hydrocarbons.—As was to be expected, alkyl sulfides cannot be estimated by the bromine water method when unsaturated hydrocarbons are present. An attempt was made to analyze a benzene solution of *n*-butyl sulfide in the presence of amylene. Twenty-five cc. of benzene containing about one per cent. of β-*n*-amylene (Eastman) was added to 25 cc. of a benzene solution of *n*-butyl sulfide (0.0500% S). This solution decolorized several times as much bromine water as that required for the oxidation of the sulfide.

The bromine water method was found applicable to a naphtha solution of *n*-butyl sulfide which was free from unsaturated hydrocarbons. "Skellysolve C," essentially normal heptane, boiling range 90 to 100°, of water white color, and sulfur free (Doctor Test), purchased from the Skelly Oil Company, was freed from a small amount of unsaturated hydrocarbons by prolonged agitation with concentrated sulfuric acid; the acid was washed out, and the naphtha steam distilled and dried. Twenty-five cc. of this purified naphtha was added to 25 cc. of a benzene solution of *n*-butyl sulfide containing 0.1000% sulfur. Duplicate analyses by the bromine water method gave results which were 0.2 and 0.4% higher than those obtained in the benzene solution alone.

Summary

1. A method has been devised for the estimation of alkyl sulfides dissolved in benzene.

2. The method is applicable to a naphtha solution free from unsaturated hydrocarbons.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME ANALYTICAL REACTIONS OF ALKYL MERCAPTANS IN BENZENE SOLUTION[1]

BY JOHN R. SAMPEY[2] AND E. EMMET REID[3]

RECEIVED APRIL 29, 1932 PUBLISHED AUGUST 5, 1932

It has been customary to estimate mercaptans by an iodimetric method.[4] In an examination of this method as applied to dilute solutions in benzene, it has been found that the time allowed for the oxidation is an important factor. The present paper describes also a study of two additional methods for the estimation of mercaptans in dilute concentrations in hydrocarbon solvents. One of these methods involves the titration of the hydriodic

[1] Presented in part before the Petroleum Division at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931, under the title "The Analysis of Mixtures of Sulfides, Disulfides and Mercaptans." This paper contains results obtained in an investigation of "Reactions of a Number of Selected Sulfur Compounds" listed as Project 28 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Fellow.

[3] Director, Project 28.

[4] Kimball, Kramer and Reid, THIS JOURNAL, **43**, 1199 (1921).

acid formed by the oxidation of the mercaptan with iodine. The second method is based upon the estimation of the hydrochloric acid produced by the action of an aqueous solution of mercuric chloride on the mercaptan.

Estimation of Mercaptans by Iodimetry.—In a study of the time required for the oxidation of mercaptans by iodine a peculiar phenomenon was observed. When exactly 50 cc. of a benzene solution of *n*-butyl mercaptan (0.0500% S) and 50 cc. of an approximately *n*/40 iodine solution were allowed to stand for twenty minutes and then titrated with a standard solution of sodium thiosulfate until the aqueous layer gave no color reaction with starch solution, it was found that less thiosulfate was required than corresponded to complete oxidation of the mercaptan to disulfide; based upon the amount of iodine apparently consumed, the calculation gave 105.9% of mercaptan oxidized. The benzene layer, however, was strongly colored with iodine, and while it was not possible to decolorize it even upon vigorous shaking with a few drops excess of thiosulfate, after several minutes the purple color appeared again in the aqueous layer, with a decrease in the intensity of the iodine color in the benzene layer. The addition of a few drops of thiosulfate solution caused only the aqueous layer to become colorless again, and to remain so for several minutes of shaking. The addition of thiosulfate was continued in small amounts until both the benzene and the aqueous layers were colorless; a calculation from the total thiosulfate consumed in the several titrations gave 99.9% oxidation to the disulfide.

In a second series of experiments an attempt was made to follow more closely the reaction between iodine and mercaptan. The same concentrations of iodine and mercaptan were used, but the titrations with thiosulfate were begun immediately, and continued at stated intervals; just enough thiosulfate was added each time to decolorize the aqueous starch layer after vigorous agitation. The results of one series of titrations are expressed in Table I.

TABLE I

RATE OF OXIDATION OF MERCAPTAN WITH IODINE

Time, min.	Thiosulfate consumed, cc.	Time, min.	Thiosulfate consumed, cc.
0	7.0	30	16.2
5	8.0	40	17.5
10	11.5	60	19.0
15	12.8	80	20.5
20	14.0	1200 (20 hrs.)	24.3

The final titration at the end of twenty hours corresponded to 99.8% oxidation of the mercaptan present. These results suggest the formation of an intermediate addition compound between the iodine and the mercaptan. This problem is being investigated further.

From a purely analytical point of view, however, it was of more impor-

tance to determine the time required for the reaction to go to completion than to follow its course in the early stages. In order to determine the minimum length of time required for the oxidation, the same concentrations of *n*-butyl mercaptan and iodine as used above were permitted to stand for forty minutes before titration; under these conditions the oxidation was 98.8% complete. From a number of analyses on the normal mercaptans from ethyl through nonyl it was found that three hours was long enough for the reaction to go to completion. Several of the secondary mercaptans, however, were discovered to oxidize much slower; for example, 50 cc. of secondary nonyl mercaptan (0.0500% S) was only 91.2% oxidized in three and one-half hours by 50 cc. of *n*/40 iodine solution. Whenever a long-chained secondary mercaptan was present, it was found best to permit twenty-four hours for the oxidation; during this period the solutions were kept in the dark to prevent the formation of iodine from the hydriodic acid produced during the oxidation.

Modification of the Iodine Method.—Two acidimetric processes for the estimation of mercaptans have been studied. The first of these involved the titration of the hydriodic acid formed during the oxidation of the mercaptan in the iodimetric method. In the second method, the hydrochloric acid liberated by the action of mercuric chloride on the mercaptan is estimated. The procedure for the estimation of the hydriodic acid may be described briefly as follows.

Exactly 50 cc. of a benzene solution of the mercaptan is allowed to stand in a glass-stoppered flask with an excess of the iodine solution until the oxidation is complete. The excess iodine is then removed with thiosulfate solution. The aqueous and benzene layers are separated, and the latter is washed with 60 cc. of water in three portions in order to free it from any hydriodic acid. The washings are added to the main aqueous layer, and the hydriodic acid is titrated with *n*/40 sodium hydroxide solution, using brom cresol purple or a purified litmus solution as indicator.

The accuracy of this method is seen in Tables II and III, where the same samples were used for the estimation of the mercaptan by the iodine and the hydriodic acid methods; the sodium hydroxide titration on each sample was performed as soon as the excess standard iodine solution had been titrated with thiosulfate solution, and the benzene layer separated and washed. The hydriodic acid method is not as accurate as the iodine method, but it was developed in the expectation that it would prove useful where the other would not apply, *e. g.*, in the estimation of mercaptans in mixtures containing unsaturated hydrocarbons.

The solutions used in Tables II and III were prepared by weighing out in a small stoppered weighing bottle the calculated amounts of mercaptans to give a liter of the specified concentration. Fifty-cc. portions of these were pipetted into glass-stoppered flasks for the analyses. The samples of the pure mercaptans were prepared by Dr. L. M. Ellis, Jr.[5]

[5] Ellis and Reid, THIS JOURNAL, **54**, 1674 (1932).

TABLE II

COMPARISON OF THE IODINE AND HYDRIODIC ACID METHODS FOR THE ESTIMATION OF MERCAPTANS

Mercaptan	S present, %	Iodine method, % S found	Iodine method, % Error	Hydriodic acid method, % S found	Hydriodic acid method, % Error
Ethyl	0.0500	0.0498	−0.4	0.0498	−0.4
	.0500	.0499	−0.2	.0500	0.0
Isopropyl	.0500	.0499	−0.2	.0500	0.0
	.0500	.0498	−0.4	.0498	−0.4
n-Butyl	.0500	.0500	0.0	.0502	+0.4
	.0500	.0499	−0.2	.0498	−0.4
Sec.-hexyl	.0500	.0501	+0.2	.0496	−0.8
	.0500	.0502	+0.4	.0497	−0.6
n-Nonyl	.0500[a]	.0506	+1.3	.0507	+1.4
	.0500[a]	.0508	+1.6	.0509	+1.8

[a] The solution of *n*-nonyl mercaptan was evidently too strong, for both methods gave high results.

TABLE III

ESTIMATION OF VARYING CONCENTRATIONS OF *n*-BUTYL MERCAPTAN

S present, %	Iodine method, % S found	Iodine method, % Error	Hydriodic acid method, % S found	Hydriodic acid method, % Error
0.2000	0.1998	−0.1	0.2020	+1.0
.2000	.2004	+0.2	.2024	+1.2
.1000	.1004	+0.4	.0989	−1.0
.1000	.1003	+0.3	.1001	+0.1
.0500	.0500	0.0	.0502	+0.4
.0500	.0499	−0.2	.0498	−0.3

Limitations of the Iodine and Hydriodic Acid Methods in the Presence of Naphthas and Unsaturated Hydrocarbons.—No complications were encountered in the determination of mercaptans in naphtha solution ("Skellysolve C") which had been freed from unsaturated hydrocarbons.[6] In the presence of amylene, however, neither the iodine nor the hydriodic acid method was applicable. An attempt was made to analyze 25 cc. of a benzene solution of *n*-butyl mercaptan (0.1000% S) to which had been added 25 cc. of a 1% amylene solution (in benzene). After this solution had stood for twenty-four hours with 50 cc. of *n*/40 iodine solution, the thiosulfate titration of the excess iodine gave an apparent sulfur content of 0.1077% due to addition of the iodine to the double bond of amylene. From the titration of the hydriodic acid only 0.0992% S was indicated. A duplicate analysis gave 0.1028% S from the iodine titration, and 0.0881% S from the hydriodic acid titration.

Mercuric Chloride Method for the Estimation of Mercaptans.—Mercaptans dissolved in benzene may be estimated rapidly through the use of an aqueous solution of mercuric chloride. Individual mercaptans have often been identified by the melting points of the salts formed from the

[6] Sampey, Slagle and Reid, THIS JOURNAL, **54**, 3401 (1932).

action of an aqueous or alcoholic solution of mercuric chloride upon a naphtha solution of the mercaptan. From the equation for the reaction

$$RSH + HgCl_2 = RSHgCl + HCl$$

it is seen that one mole of acid is liberated for each mole of mercaptan. The method of analysis based upon the titration of the acid may be indicated as follows.

Fifty cc. of a benzene solution of the mercaptan (0.0500% S) is shaken vigorously for three minutes with 25 cc. of a 1% aqueous solution of mercuric chloride; the amount of the mercury salt which precipitates varies with the individual mercaptan; the higher secondary mercaptans give salts which are completely soluble in the 50 cc. of benzene. In the event no precipitation takes place, or only a slight precipitate is formed, the two layers are separated and the hydrochloric acid is washed from the benzene with three 25-cc. portions of water; the acid in the aqueous layer and the washings is titrated with $n/40$ sodium hydroxide, using methyl orange or methyl red as indicator. When a heavy precipitate is formed by the mercuric chloride it is better not to attempt a separation of the two layers, but to add the alkali to the mixture slowly with frequent shakings; methyl orange must be used in this case, for methyl red dissolves in the benzene and becomes orange colored even when there is acid in the aqueous layer; since methyl orange is more soluble in the aqueous layer, and the white precipitate of RSHgCl remains in the benzene layer, the end-point is almost as sharp as when the layers are separated.

Calculations from the preliminary titrations gave results which were low. This was to be expected since both methyl orange and methyl red change color on the acid side. It was necessary to use this type of indicator, however, in order to prevent the formation of $Hg(OH)_2$. It was found possible to apply a correction factor by standardizing against $n/40$ hydrochloric acid a volume of sodium hydroxide approximately the same as that required in the titration after the mercuric chloride treatment of the mercaptan. The values obtained in the standardization with hydrochloric acid when methyl orange and methyl red were the indicators were 0.4 to 0.5 cc. lower than the results when brom cresol purple and purified litmus were the indicators.

Table IV gives the results of the analyses of benzene solutions of mercaptans.

TABLE IV

MERCURIC CHLORIDE METHOD FOR THE ESTIMATION OF MERCAPTANS

Mercaptan	S present, %	S found, %
Ethyl	0.0500	0.0503
Isopropyl	.0500	.0498
n-Butyl	.0500	.0499
n-Butyl	.1000	.1003
n-Butyl	.2000	.2006
Sec.-butyl	.0500	.0501
n-Heptyl	.0500	.0496
Sec.-nonyl	.0500	.0503

Limitations of the Mercuric Chloride Method in the Presence of Naphthas and Unsaturated Hydrocarbons.—The mercuric chloride

method was applied without difficulty to *n*-butyl mercaptan in a naphtha ("Skellysolve") which was free from unsaturated hydrocarbons. In the presence of the latter, however, the method failed. Hofmann and Sand[7] were the first to discover that mercuric chloride liberates hydrochloric acid when shaken with an unsaturated hydrocarbon of the olefin series. Several cubic centimeters of alkali was required to neutralize the acid when a 1% mercuric chloride solution was shaken for three minutes with a 1% solution of amylene in benzene.

Summary

1. The iodimetric method for the estimation of mercaptans has been applied to benzene solutions.

2. Two acidimetric methods for the estimation of mercaptans are given: in one the hydriodic acid formed in the iodimetric oxidation is titrated; in the second method, the hydrochloric acid liberated by the action of mercuric chloride on the mercaptan is estimated.

[7] Hofmann and Sand, *Ber.*, **33,** 1349 (1900).

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE PROPERTIES OF *d*-MANNURONIC ACID LACTONE

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

RECEIVED MAY 2, 1932 PUBLISHED AUGUST 5, 1932

Since the publication of our paper on the isolation and identification of *d*-mannuronic acid lactone from *Macrocystis pyrifera*,[1] the lactone has been obtained in this Laboratory by hydrolysis of alginic acid from *Fucus serratus* and *Laminaria saccharina*.[2] As a result of our further work, we have discovered the mutarotation of the lactone which escaped our observation because of the small amount of the substance available in our earlier experiments.

The lactone was isolated through the cinchonine salt as previously described.[1] The melting point and optical rotation of the cinchonine salt from *Fucus serratus* and *Laminaria saccharina* agreed with the values reported for the salt from *Macrocystis pyrifera*.[3] Under different conditions of hydrolysis, however, Schmidt and Vocke,[4] Miwa[5] and Bird and Haas[6] have obtained salts with different properties.

[1] Nelson and Cretcher, THIS JOURNAL, **52,** 2130 (1930).

[2] We are indebted to Dr. E. J. Allen, Director of the Marine Biological Station, Plymouth, England, for his kindness in supplying us with these algae.

[3] Cretcher and Nelson, *Science*, **67,** 537 (1928); Nelson and Cretcher, THIS JOURNAL, **51,** 1914 (1929).

[4] Schmidt and Vocke, *Ber.*, **59,** 1585 (1926).

[5] Miwa, *J. Chem. Soc. Japan*, **51,** 738 (1930).

[6] Bird and Haas, *Biochem. J.*, **25,** 403 (1931).

TABLE I

CINCHONINE SALTS OF URONIC ACIDS FROM ALGIN

		M. p., °C.	$[\alpha]_D$
Nelson and Cretcher	*Macrocystis pyrifera*	152	+113.6°
	Fucus serratus	153	+114.3°
	Laminaria saccharina	152	+111.2°
	From crystalline mannuronic lactone	154	+113.3°
Schmidt and Vocke	*Fucus serratus*	204	
Miwa	*Ulopteryx pinnatifidia* and other algae	174	+140.3°
Bird and Haas	*Laminaria*	195–197	+112.8°
		161	+154°

These discrepancies seem to indicate the presence of more than one uronic acid in alginic acid[7] but we believe it is more probable that they are due to differences in degree of hydrolysis. The presence of glucuronic acid has been suggested[4,8] but has never been established. We have prepared cinchonine mannuronate from crystalline mannuronic lactone and have found that the melting point and specific rotation of this preparation closely check these properties of the cinchonine salt obtained by us after hydrolysis of alginic acid.

The preparation of the cinchonine salt of mannuronic acid after hydrolysis of alginic acid is a matter of considerable trouble. This salt is not a suitable derivative for the characterization of mannuronic acid. The cinchonidine and brucine salts are more easily crystallized and their properties are described in the experimental part.

The separation of the barium salts of the products of hydrolysis of alginic acid by fractional precipitation with alcohol is a convenient method of isolating mannuronic acid. Schoeffel and Link[9] have recently applied this method in their study of the preparation of mannuronic lactone.[10]

Experimental Part

Preparation of *d*-Mannuronic Lactone.—Hydrolysis of alginic acid from *Macrocystis pyrifera*, *Fucus serratus* and *Laminaria saccharina* with 80% sulfuric acid and the subsequent steps in the preparation of the lactone were accomplished with few changes from our previously described procedure.[1,3] Among these was the method of removing sul-

[7] It has been established that alginic acid is a uronic acid polymer exclusively.[3]

[8] Atsuki and Tomodo, *J. Soc. Chem. Ind.* (*Japan*), **29**, 509 (1926).

[9] Schoeffel and Link, *J. Biol. Chem.*, **95**, 213 (1932).

[10] Schoeffel and Link state that they obtained a "pure" barium salt after precipitation of polymers with alcohol. The barium content of their preparation was between 26 and 27% (calcd. 26.26%). Without an intimation that their salt was not pure barium mannuronate it may be stated that within the limits of analysis given the presence of a considerable amount of polymers is possible. Conclusions as to the purity of the barium salt may better be based on determination of its reducing power. It has been shown[1] that the lactone is abnormal in its reaction with iodine in alkaline solution (Willstätter–Schudell), but recent determinations in this Laboratory show that it is possible to obtain satisfactory estimations of the lactone with Benedict's solution.

furic acid after hydrolysis. In order to reduce decomposition of the uronic acid, it was found advisable to remove most (90%) of the inorganic acid with barium hydroxide at room temperature and the remainder with an excess of barium carbonate from the hot solution. The solution was concentrated and cooled to remove the more insoluble barium salts and the cinchonine salt was prepared from the filtrate. At times the cinchonine salt was difficult to crystallize. Several extractions of the aqueous solution with chloroform were found to be indispensable. Then the solution was evaporated to a thick sirup and allowed to crystallize in a cooler. The solid mass of salt was broken up and washed with 95% alcohol and filtered on a Büchner funnel.

The crystallization of the lactone from glacial acetic acid was sometimes attended with difficulty. Frequently a gummy substance precipitated while the acetic acid extract of the lactone was cooling. In these cases the crystalline lactone was obtained by decanting the mother liquor and concentrating to a small volume in a vacuum desiccator containing sodium hydroxide. The maximum yield of lactone recovered from the cinchonine salt was 35% of the theoretical. Improvements in the process, particularly the use of other alkaloids, will be investigated in this Laboratory.

The pure lactone is white, without the pink tinge of color usually apparent in the product from the first crystallization. The lactone is deposited from glacial acetic acid in dense clusters at the border of which may be seen, under a high power lens, the projecting ends of crystals of not easily recognizable form. The lactone obtained from *Macrocystis pyrifera*, *Laminaria saccharina* and *Fucus serratus*, after one recrystallization from glacial acetic acid, possessed the same melting point, 139°, which did not change on three further recrystallizations, and (within the limit of experimental error) the same maximum rotation

$$[\alpha]_D^{22}\ +93.8^\circ\ (\textit{Macrocystis pyrifera})$$
$$[\alpha]_D^{20}\ +93.8^\circ\ (\textit{Laminaria saccharina})$$
$$[\alpha]_D^{20}\ +93.6^\circ\ (\textit{Fucus serratus})$$

In all cases the mutarotation was of the character described in the following paragraph.

Mutarotation of *d*-Mannuronic Acid Lactone.—The lactone obtained from *Macrocystis pyrifera* was recrystallized four times from glacial acetic acid as follows. The lactone was dissolved in the minimum amount of solvent heated in a boiling water-bath. The solution was allowed to cool until there was a slight precipitate, quickly filtered on a vacuum filter and allowed to crystallize overnight. After the final crystallization, the lactone was washed several times with absolute alcohol and anhydrous ether and dried. The following table shows the rotation of 0.1892 g. of the recrystallized lactone in 10.08 cc. of aqueous solution. A 1-dm. tube was used. The first recorded specific rotation (three minutes after solution) was $[\alpha]_D^{22}$ +79.9°. The rotation increased rapidly to the maximum, $[\alpha]_D^{22}$ +93.8°, twenty-eight minutes after solution and then slowly decreased. The stoppered tube (with a drop of toluene on the surface of the solution) was allowed to stand at room temperature for 864 hours, at which time the rotation was not constant.

TABLE II

MUTAROTATION OF *d*-MANNURONIC LACTONE

Hours	α_D	$[\alpha]_D$	Hours	α_D	$[\alpha]_D$
0.05	+1.50	+79.9	24	1.74	92.7
.13	1.65	87.9	168	1.66	88.4
.22	1.72	91.6	336	1.58	84.2
.30	1.74	92.7	504	1.44	76.7
.38	1.75	93.2	672	1.30	69.3
.47	1.76	93.8	864	1.16	61.8

The rapid initial increase is probably due to attainment of equilibrium between the α and β forms of the aldehyde and the subsequent decrease is due to the formation of mannuronic acid. It was found by titration that the solution contained 39.1% acid and 60.9% lactone when the specific rotation was +61.8°. Using these data for an approximate calculation of the equilibrated rotation of *d*-mannuronic acid gives $[\alpha]_D$ +12.0°. It may be noted that this value is close to the equilibrium rotation of *d*-mannose, $[\alpha]_D$ +14.6°.

The equilibrium ratio of acid and lactone was determined by heating solutions of the lactone at 80°. The percentages of acid and lactone, respectively, were 59.6 and 40.4 after 19.5 hours at 80°. Longer heating did not change this ratio appreciably, but caused a decrease of the optical rotation. Decomposition was evident after heating for thirty-five hours, when the solution became yellow.

Cinchonine Mannuronate.—0.110 g. of mannuronic lactone was dissolved in 20 cc. of 50% alcohol and heated with a slight excess of cinchonine in a water-bath at 80° for two hours. The solution was evaporated under reduced pressure to remove alcohol. Water was added and the solution was filtered to remove a small amount of cinchonine, extracted twice with chloroform and evaporated under reduced pressure to a thick sirup. The salt crystallized before cooling. It was dissolved in 80% alcohol and crystallized by evaporation in a desiccator under reduced pressure to a small volume. After washing with cold 80% alcohol, absolute alcohol and ether, it was dried over phosphorus pentoxide under reduced pressure. 0.106 g. of pure white salt was obtained. The salt crystallizes in sheaves of slender rectangular plates and when dry is quite insoluble in cold water. The melting point was 154°, with decomposition. 0.0285 g. in 3.017 cc. of aqueous solution gave an observed rotation of +1.07° in a 1-dm. tube; $[\alpha]_D^{24}$ +113.3°.

Cinchonidine Mannuronate.—Prepared in the same manner as the cinchonine salt and crystallized twice from 95% alcohol. After washing with absolute alcohol and ether, it was dried in a vacuum over phosphorus pentoxide. From 0.090 g. of lactone 0.140 g. of pure white salt was obtained. The compound crystallizes in small clusters of radiating needles and melts with decomposition at 154°.

0.0393 g. in 3.017 cc. of aqueous solution gave an observed rotation of −1.02° in a 1-dm. tube; $[\alpha]_D^{24}$ −78.3°.

Anal. (Micro Dumas) Calcd. for $C_{25}H_{32}O_8N_2$: N, 5.73. Found: N, 5.42, 5.43.

Brucine Mannuronate.—Prepared in the same manner as the cinchonine salt and crystallized twice from 80% alcohol. 0.070 g. of buff colored salt was obtained from 0.080 g. of lactone. The compound crystallizes in irregular masses of small needles and melts at 147° with decomposition. 0.0352 g. in 3.017 cc. of aqueous solution gave an observed optical rotation of −0.27° in a 1-dm. tube; $[\alpha]_D^{24}$ −23.1°.

Anal. (Micro Dumas). Calcd. for $C_{29}H_{36}O_{11}N_2$: N, 4.76. Found: N, 4.42, 4.47.

Summary

d-Mannuronic lactone has been isolated for the first time from the alginic acid of *Laminaria saccharina* and *Fucus serratus*. Data on the mutarotation of the lactone are presented and an approximate value for the rotation of the equilibrated mixture of α- and β-forms of the free acid has been calculated. The preparation and properties of the cinchonine and the more easily crystallized brucine and cinchonidine salts of *d*-mannuronic acid are described.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND FIXED NITROGEN DIVISION OF THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE SYNTHESES OF 2-IMIDAZOLONE-4-CARBOXYLIC ACID AND 2-IMIDAZOLONE

BY GUIDO E. HILBERT

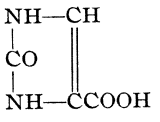
RECEIVED MAY 5, 1932 PUBLISHED AUGUST 5, 1932

Davidson and Baudisch[1] have utilized the von Pechmann reaction[2] for a novel synthesis of uracil by treating malic acid and urea with fuming sulfuric acid. More recently, Hilbert[3] in a similar manner prepared uracil-4-acetic acid from citric acid and urea. This method for the synthesis of cyclic ureides by condensing urea with a derivative of formylacetic acid, which is formed by the action of sulfuric acid on an α-hydroxy-α,β-dicarboxylic acid, is practical only when the hydroxy acid is easily available. One other analog, tartaric acid, immediately suggests itself and the study of the product prepared from it and urea in sulfuric acid is the subject of this investigation.

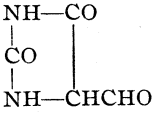
The initial product formed in a reaction between tartaric and sulfuric acids would be expected to be α,β-dihydroxyacrylic acid (1) (formylglycolic acid)

$$(HO)CH{=}C(OH)COOH \qquad (I)$$

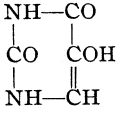
which upon subsequent reaction with sulfuric acid would yield glyoxal. The reaction of the degradation product of tartaric acid with urea can theoretically lead to a number of products. The condensation of urea with the α- and β-hydroxy groups of (I) would be expected to yield 2-imidazolone-4-carboxylic acid (II) and the combination with either the α- or β-hydroxy and the carboxyl group would be expected to produce 5-formylhydantoin (III) and isobarbituric acid (IV), respectively. A reaction between glyoxal and urea would yield acetylenediureide (V).



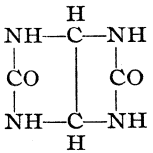
(II)



(III)



(IV)



(V)

Because of the presence of the additional α-hydroxy group, it is difficult to predict which product will be formed. The cases, involving malic and citric acids are much simpler since each can yield only one cyclic nitrogen compound.

[1] Davidson and Baudisch, THIS JOURNAL, **48**, 2379 (1926).

[2] Von Pechmann, *Ber.*, **17**, 936 (1884); *Ann.*, **264**, 261 (1891).

[3] Hilbert, THIS JOURNAL, **54**, 2076 (1932).

The action of fuming sulfuric acid upon tartaric acid and urea actually leads to the formation of only one product which, considering the experimental conditions, is obtained in a satisfactory yield. It melts with decomposition at 261°, is insoluble in organic solvents, and slightly soluble in boiling water. The analytical results indicate that the empirical formula is $C_4H_4O_3N_2$ which is that required by the isomers (II), (III), and (IV), and which definitely eliminates (V) from consideration. The possibility that the product is isobarbituric acid is excluded by the wide difference in the decomposition points and by the fact that the product neither responds to the Wheeler-Johnson color test[4] nor gives the characteristic blue color[5] with ferric chloride. Of the two remaining, 2-imidazolone-4-carboxylic acid (II) was shown to be more probable since the product is easily soluble in an aqueous solution of potassium carbonate.

The experimental evidence obtained by degradation and by conversion into derivatives definitely shows that the product is 2-imidazolone-4-carboxylic acid. It has a neutral equivalent of 121 (calcd. 128) and on appropriate treatment with sulfuric acid and alcohol forms an ester. Oxidation with chromic acid leads to the formation of parabanic acid, which is excellent evidence for the original presence of the imidazole ring.[6] Methylation with dimethyl sulfate in aqueous sodium hydroxide yields 1,3-dimethyl-2-imidazolone-4-carboxylic acid (decomp. 229–230°), which, by a comparison of the properties, appears to be similar to that prepared by the hydrolysis of 7,8-dimethyldihydrouric acid (decomp. 220°)[7] and by the hydrolysis of 1,3-dimethyl-5-aminouracil-4-carboxylic acid (decomp. 224–225°).[8] In order to obtain additional evidence that the methylated imidazolone carboxylic acid is the same as that reported by Biltz and Bülow, their work on the decarboxylation was repeated. The properties of the resulting 1,3-dimethyl-2-imidazolone are quite similar to those previously described.

2-Imidazolone-4-carboxylic acid reacts with acetic anhydride and yields a crystalline product which does not melt at 300°. As it is either sparingly soluble or insoluble in all ordinary solvents it is impossible to determine its molecular weight. The empirical formula is either $C_6H_4O_3N_2$ or a multiple of this. Its striking behavior toward alkali indicates that it

[4] Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).

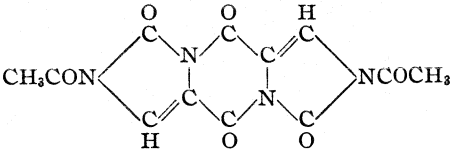
[5] Behrend and Roosen, *Ann.*, **251**, 235 (1889).

[6] The formation of parabanic acid by oxidation does not always necessarily indicate the original presence of an imidazole ring; see for example the oxidation of 1,4-dimethyluracil by Henkel, *Ann.*, **378**, 170 (1911), to 1-methylparabanic acid. A similar alteration in the ring is impossible in the present case since the presence of one of the carbon atoms in a carboxyl group does not allow a sufficient number to remain to form a pyrimidine ring.

[7] Biltz and Bülow, *Ann.*, **457**, 117 (1927).

[8] Beythien, *ibid.*, **389**, 214 (1912).

may be the diketopiperazine (VI). On treatment with potassium hydroxide the acetyl groups are removed and a crystalline canary yellow potassium salt forms, which analyzes well for $C_8H_2N_4O_4K_2$.

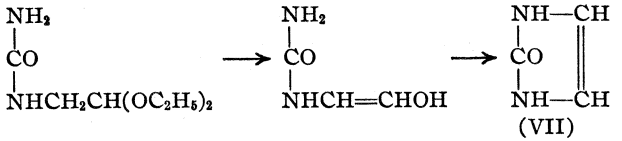


(VI)

The condensation of urea with the hydroxyl groups of α,β-dihydroxyacrylic acid, in preference to a reaction involving the carboxyl group, is very interesting and not without analogy. Certain rare rearrangements of pyrimidines to imidazolones seem to undergo a similar reaction. Beythien[8,9] for example, prepared 1,3-dimethyl-2-imidazolone-4-carboxylic acid from 1,3-dimethyl-5-aminouracil-4-carboxylic acid, and Johnson and Hadley[10] noted the transformation, on alkaline treatment, of 4-(α-hydroxyl ethyl)-uracil to 4,5-dimethyl-2-imidazolone. These pyrimidines are apparently hydrolyzed to form the open-chain urea derivatives in which the hydroxyl group combines with the amino radical to yield the imidazolone.

It is unfortunate that there is no method for the reduction of a lactam such as occurs in 2-imidazolone-4-carboxylic acid. All efforts toward this end resulted in failure. A successful means of reduction would have considerable significance as it would allow an easy method of entrance into the important imidazoline series of compounds.

The Synthesis of 2-Imidazolone.—The synthesis of 2-imidazolone has been reported twice in the literature. The properties of the product obtained, however, were quite different. Marckwald[11] by the hydrolysis of acetalylurea with dilute sulfuric acid isolated a product to which he assigned the structure of 2-imidazolone (VII).



(VII)

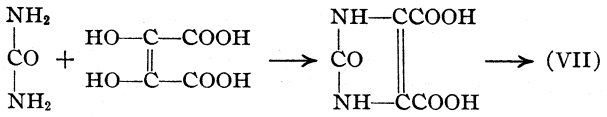
It was reported to be a semi-crystalline substance which did not melt at the boiling point of sulfuric acid. All attempts to convert this into some derivative were unsuccessful. Later Fenton and Wilks[12] by the condensation of dihydroxymaleic acid with urea obtained a crystalline product which decomposed at 245° and yielded a monoacetyl derivative.

[9] See also Bremar, *ibid.*, **378**, 188 (1911).

[10] Johnson and Hadley, THIS JOURNAL, **39**, 1715 (1917).

[11] Marckwald, *Ber.*, **25**, 2357 (1892).

[12] Fenton and Wilks, *J. Chem. Soc.*, **95**, 1329 (1909).



The analytical results and the molecular weight determination agreed well for 2-imidazolone. A direct comparison of this with Marckwald's compound definitely showed that they were different. Since Marckwald's substance was made by a more direct method, Fenton and Wilks apparently believed that he had obtained the true 2-imidazolone and accordingly named theirs "iso-imidazolone."

In order to throw further light on this question, 2-imidazolone-4-carboxylic acid was decarboxylated. This was effected by heating the acid at a temperature of 220° in a vacuum. The 2-imidazolone sublimed on the cooler parts of the vessel in the form of pyramidal crystals that decomposed at 250–251°. It had all the properties of the compound described by Fenton and Wilks, with the exception that it did not give a Weidel color reaction. The similarity of the chemical and optical properties and the fact that it also yielded an acetyl derivative melting at the same temperature as that of "iso-imidazolone" would seem to warrant the conclusion that these substances are identical and that Fenton and Wilks were the first to have obtained 2-imidazolone. The carbon and hydrogen values obtained by Fenton and Wilks for the acetyl derivative led them to believe that it was 1-acetyl-2-imidazolone. The product obtained in the present investigation, however, has been definitely shown to be 1,3-diacetyl-2-imidazolone.

I am indebted to Dr. David Davidson for a discussion concerning this work. The analytical results recorded were kindly carried out by Dr. Reid T. Milner and Mrs. Mildred S. Sherman.

Experimental Part

Preparation of 2-Imidazolone-4-carboxylic Acid.—A series of experiments run under varying conditions was carried out and the following procedure was found to be the best. To a 2-liter three-necked flask fitted with a stirrer was added 400 cc. of 13% fuming sulfuric acid. After cooling this to 0°, 112 g. of finely powdered anhydrous tartaric acid was added at such a rate that the temperature did not rise above 10°—this required ten minutes. The ice-bath was removed and 100 g. of urea added. The temperature during this operation rose rapidly and was finally held with the aid of a burner at 80° for thirty minutes. A vigorous reaction ensued with the concomitant evolution of carbon monoxide and carbon dioxide; the reaction mixture rapidly turned black. After completion of the reaction the contents of the flask were cooled and poured on 1200 g. of ice. An amorphous chocolate colored precipitate immediately separated. This, having stood in the ice box overnight, was filtered; yield of crude dry product, 35 g. It was decolorized by boiling a water solution with large portions of bone black and finally recrystallizing from water from which it separated as colorless nodules; it melted with vigorous effervescence at 261°. 2-Imidazolone-4-carboxylic acid was slightly soluble in boiling water and insoluble in organic solvents.

Anal. Calcd. for $C_4H_4O_3N_2$: C, 37.50; H, 3.15; N, 21.88. Found: C, 37.95; H, 3.28; N, 21.98, 21.85.

The acid was dissolved in an excess of standardized sodium hydroxide and titrated back with standardized hydrochloric acid using phenolphthalein as the indicator.

Neutral equivalent. Subs., 0.1164, 0.0489: 14.06, 5.78 cc. of 0.0694 *N* NaOH. Calcd. for $C_3H_3N_2OCOOH$: 128. Found: 119.3, 121.9.

On treating the acid with Tollens' reagent it formed a silver mirror. The same result was obtained by heating it with an ammoniacal solution of silver nitrate. A water solution of the acid yielded a dark brown color when treated with aqueous ferric chloride. It did not give a Weidel color reaction.

In order to obtain evidence concerning the structure of 2-imidazolone-4-carboxylic acid, its action toward various reagents was studied. The following did not yield satisfactory results. A water solution of the acid was treated with bromine. The water was removed and a pale yellow sirup resulted which did not crystallize on standing, and was not further investigated. Treatment of the imidazolone with phosphorus oxychloride led to complete decomposition. On evaporation to dryness with fuming hydrochloric acid a gummy residue resulted that was not amenable to the isolation of a homogeneous product.

Isobarbituric acid was shown neither to be an intermediate in the formation of the imidazolone nor to be susceptible to rearrangement. It was heated with both dilute and concentrated sulfuric acid, 12% fuming sulfuric acid, 48% hydrobromic and 20% sodium hydroxide and in every case was recovered unaltered.

Oxidation of 2-Imidazolone-4-carboxylic Acid to Parabanic Acid.—To a suspension of 1 g. of 2-imidazolone-4-carboxylic acid in 20 cc. of water was added 1 g. of sodium dichromate and 3 g. of concentrated sulfuric acid. A vigorous evolution of carbon dioxide took place. After this had slowed down the green reaction mixture was boiled for fifteen minutes, another gram of sodium dichromate added, and the heating continued on a steam-bath for an hour; the imidazolone gradually dissolved. After cooling, the solution was thoroughly extracted with 4 portions of 40 cc. of ether. The ether extract was washed with a small amount of water and dried with calcium chloride. The ether was removed by distillation and the parabanic acid remained as a colorless crystalline cake; yield, 0.28 g. After recrystallization from 2 cc. of water, from which it separated in the form of curved thin plates, it decomposed at 247° with effervescence. It was shown to be identical with an authentic specimen of parabanic acid.[13]

Ethyl-2-imidazolone-4-carboxylate.—The usual method of esterification, in which the acid is treated with alcohol in the presence of a small quantity of sulfuric acid, was unsuccessful in this case probably because of the insolubility of the imidazolone in alcohol.

The following procedure was found to give the best results. Seven grams of 2-imidazolone-4-carboxylic acid was dissolved in 17 cc. of concd. sulfuric acid by heating in an oil-bath to 115°. Upon adding 40 cc. of absolute ethyl alcohol, the dark brown solution was heated at 100° for three hours, allowed to stand overnight, and poured on 80 g. of ice. A pale yellow flocculent solid separated immediately. The mixture was cooled in an ice–salt bath and filtered. The ester was recrystallized several times from

[13] From a survey of the literature the simplest method for the preparation of parabanic acid appears to be that of Michael, *J. prakt. Chem.*, [2] **35**, 457 (1887). This involves the condensation of urea with ethyl oxalate in the presence of sodium ethylate. A white precipitate immediately forms which was reported to be the sodium salt of parabanic acid (no analysis given). This reaction has been reinvestigated and definitely shown not to yield parabanic acid.

95% alcohol, from which it separated as colorless glistening plates, melting at 255°; yield, 50% of the theoretical. It was slightly soluble in boiling alcohol and insoluble in water.

Anal. Calcd. for $C_6H_8O_3N_2$: C, 45.84; H, 5.13; N, 17.95. Found: C, 46.14, 46.06; H, 5.17, 5.46; N, 18.13, 17.95.

Attempts to reduce the double bond in this compound by the Adams–Shriner method were unsuccessful.

1,3-Dimethyl-2-imidazolone-4-carboxylic Acid.—Five grams of 2-imidazolone-4-carboxylic acid was dissolved in a solution of 10 g. of sodium hydroxide in 30 cc. of water. This was cooled in an ice bath and 15 g. of dimethyl sulfate slowly added with stirring. A vigorous reaction took place with the evolution of heat. After this had practically ceased, the reaction mixture was made strongly alkaline with 20% sodium hydroxide and warmed on the steam-bath for one hour. It was filtered from a small amount of black flocculent material and then acidified with hydrochloric acid. On cooling, a mass of colorless needles separated which melted at 207–215°. It was impossible to raise the melting point by recrystallization. As the product was obviously still impure it was again subjected to methylation. This time, after decolorizing with bone black and recrystallizing from water, it separated as long colorless needles and melted sharply at 229–230° with effervescence; yield 4 g.

Anal. Calcd. for $C_6H_8O_3N_2$: C, 46.14; H, 5.17; N, 17.95. Found: C, 46.39; H, 5.05; N, 17.84, 17.95.

Conversion of 1,3-Dimethyl-2-imidazolone-4-carboxylic Acid to 1,3-Dimethyl-2-imidazolone.—One gram of 1,3-dimethyl-2-imidazolone-4-carboxylic acid was heated at its melting point until effervescence ceased. The colorless liquid on cooling and scratching solidified to a mass of dendritic crystals. The product was very hygroscopic, making it difficult to get either a good melting point or an analysis. It had all the properties of the substance reported by Biltz and Bülow, with the exception that it did not give the initial violet color reaction upon treatment with bromine. A water solution of the product obtained in this work immediately decolorized bromine water without undergoing any intermediate color change. It is possible that Biltz's product was slightly contaminated with an impurity.

Treatment of 2-Imidazolone-4-carboxylic Acid with Acetic Anhydride.—To 200 cc. of acetic anhydride was added 1.8 g. of the imidazolone and the mixture refluxed. After heating for one hour, a pale yellow solution resulted. On cooling and standing overnight, star-like clusters of colorless prisms separated; these were removed by filtration. The filtrate on concentration deposited a finely divided pale brown solid which proved to be identical with the above crystalline material. It was very slightly soluble in boiling acetic acid and acetic anhydride and insoluble in other organic solvents; it did not melt at a temperature of 300°. The product for analysis was boiled with acetic acid, filtered and well washed.

Anal. Calcd. for $C_{12}H_8O_6N_4$: C, 47.35; H, 2.65; N, 18.43. Found: C, 47.49, 47.49; H, 2.91, 2.72; N, 18.08, 18.24 (Kjeldahl).

The most striking property of this substance was that on treatment with a solution of potassium hydroxide or potassium carbonate, it was converted into a yellow potassium salt. Recrystallization from water, in which it was quite soluble, yielded yellow needle-like blades that charred at a temperature considerably above 300°.

Anal. Calcd. for $C_8H_2N_4O_4K_2$: C, 32.41; H, 0.68; N, 18.91; K, 26.40. Found: C, 32.46, 32.69; H, 1.31, 1.00;[14] N, 18.45, 18.52; K, 26.04.

[14] The percentage of hydrogen is so low that the values obtained are probably not very significant.

A water solution of the salt on acidification with hydrochloric acid precipitated a colorless solid which did not melt at 300°.

2-Imidazolone.—The application of the usual methods for the decarboxylation of an acid to 2-imidazolone-4-carboxylic acid was unsuccessful. Direct heating at atmospheric pressure was impractical owing to the fact, as later found out, that the acid melted with decomposition above the decomposition point of 2-imidazolone. The experiments in which the acid was heated in some medium such as diphenylmethane led to an amorphous brown product from which nothing crystalline could be isolated. It was finally found that heating the acid in a vacuum yielded a generous amount of 2-imidazolone. Under these conditions, the imidazolone, as soon as it was formed, sublimed to the cooler part of the flask and thus was removed from the heated zone.

One gram of finely powdered 2-imidazolone-4-carboxylic acid in a round-bottomed flask with a long wide neck was heated in an oil-bath at 220° for six hours at 2 mm. pressure. Glistening crystals were gradually deposited on the neck of the flask; yield, 0.45 g. It was recrystallized from 1 cc. of boiling water from which it separated as dendrites of pyramidal crystals. 2-Imidazolone colors at 225° and decomposes to a red liquid at 250–251° (corr.).

Anal. Calcd. for $C_3H_4ON_2$: C, 42.84; H, 4.80; N, 33.33. Found: C, 42.89; H, 5.08; N, 33.18.

It gives the dark red color reaction with aqueous ferric chloride previously described by Fenton and Wilks. It does not, however, give the Weidel color reaction. As this test is very sensitive and as it has never before been reported to be given by imidazolones, it would appear that the observation of the English investigators was probably due to the presence of a small amount of an impurity. The pink color reaction with hydrochloric acid and hydrogen peroxide, also described by Fenton and Wilks, is extremely faint, so faint that it can hardly be classified as being a significant property of 2-imidazolone.

Fenton and Wilks reported the results of a crystallographic examination of their crystals. A cursory examination of the crystals obtained by the decarboxylation of 2-imidazolone-4-carboxylic acid indicated that they were apparently uniaxial, optically negative and highly birefringent. They possibly have a lower symmetry than that of the tetragonal system, and appear to be identical with those described by Fenton and Wilks.

1,3-Diacetyl-2-imidazolone.—The acetyl derivative was made in the same manner as described by Fenton and Wilks. The easiest method of purification was that of sublimation. It occurs as long silky needles melting at 105–106°.

Anal. Calcd. for $C_7H_8O_2N_2$: C, 49.98; H, 4.80; N, 16.67. Found: C, 49.92, 49.71; H, 4.72, 4.74; N, 16.75, 16.61.

Fenton and Wilks reported a melting point of 106°. The percentages of carbon and hydrogen found by them were 48.07 and 5.00 (calcd. 47.62 and 4.76), respectively. Unfortunately the analysis for nitrogen, which would have been more significant, was not made. It seems reasonable to believe that Fenton and Wilks were dealing with the diacetyl derivative and that their analysis for carbon was somewhat low.

Summary

1. Urea and tartaric acid in fuming sulfuric acid yield 2-imidazolone-4-carboxylic acid. Its structure was proved and a number of derivatives prepared.

2. The synthesis of 2-imidazolone was effected by the decarboxylation of 2-imidazolone-4-carboxylic acid. It is probably identical with the "iso-imidazolone" of Fenton and Wilks.

WASHINGTON, D. C.

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

ALCOHOLYSIS AND HYDROLYSIS OF 1,3-DIKETONES AND BETA-KETO ESTERS

BY RALPH CONNOR AND HOMER ADKINS

RECEIVED MAY 9, 1932 PUBLISHED AUGUST 5, 1932

A 1,3-diketone such as diacetylmethane does not undergo alcoholysis, as indicated in equation I, at temperatures obtainable in the liquid phase at atmospheric pressure unless a catalyst is used.

$$CH_3COCH_2COCH_3 + C_2H_5OH = CH_3CO_2C_2H_5 + CH_3COCH_3 \qquad (I)$$

Hydrogen chloride and sodium ethoxide are active in bringing about this reaction but it is necessary to use high concentrations of the so-called catalyst in order to obtain a reasonably rapid rate of alcoholysis. For example, one hundred hours were required at 60° in order to completely cleave diacetylmethane even when the ratio of hydrogen chloride to diketone was 1 to 3.[1] The necessity for these high concentrations of catalyst indicates very clearly that hydrogen chloride as well as sodium ethoxide form compounds with the diketone or ester or both, to such an extent that the course of the cleavage may be profoundly modified. That the course of the reaction is modified by the environment during cleavage is further evidenced by the variation in the ratio of the two alternative modes of cleavage of an unsymmetrical 1,3-diketone as indicated in equations II and III.[2]

$$CH_3COCH_2COC_4H_9 + C_2H_5OH \longrightarrow CH_3CO_2C_2H_5 + CH_3COC_4H_7 \qquad (II)$$

$$\searrow\ C_4H_9CO_2C_2H_5 + CH_3COCH_3 \qquad (III)$$

These considerations, in conjunction with the fact that no conditions were found under which β-keto esters underwent alcoholysis in the presence of hydrogen chloride, led to a search for conditions under which 1,3-diketones and β-ketonic esters would undergo alcoholysis even in the absence of any added catalyst. Conditions suitable for such an alcoholysis were suggested by the finding[3] that dehydroacetic acid showed a 70% alcoholysis at 190° after two hours, the product being acetoacetic ester (not acetoacetic acid as indicated in the table on p. 5195 of the paper just cited). Since dehydroacetic acid is a 1,3-diketone as well as a di-β-keto ester, this result suggests what is now known to be true, *i. e.*, that the diketones may be split under conditions which leave β-keto esters unaffected.

Alcoholysis of 1,3-Diketones.—The alcoholysis of diacetyl- and dibenzoylmethanes and of five unsymmetrical acetylmethanes (*i. e.*, *n*-valeryl, isovaleryl, trimethylacetyl, cyclohexanoyl and benzoyl) has been

[1] Adkins, Kutz and Coffman, THIS JOURNAL, **52**, 3213 (1930).

[2] Kutz and Adkins, *ibid.*, **52**, 4036 (1930).

[3] Adkins, Connor and Cramer, *ibid.*, **52**, 5194 (1930).

studied at 150–250° under about 100 atmospheres' pressure, using (1) alcohol which had been dried over lime and sodium ethoxide, (2) alcohol which had been dried over lime only and (3) alcohol which contained 0.2% of aluminum ethoxide. A summary of the results has been given in Table I along with the results obtained by Kutz[2] in the alcoholysis of the same diketones using hydrogen chloride as a catalyst at 60° and atmospheric pressure.

TABLE I

ALCOHOLYSIS OF 1,3-DIKETONES[a]

Diketone	EtOH (Dry)[b] % Alcoholysis	EtOH (Dry)[b] % CH_3CO	EtOH (Moist)[c] % Alcoholysis	EtOH (Moist)[c] % CH_3CO	EtOH + Al(OEt)$_3$[d] % Alcoholysis	EtOH + Al(OEt)$_3$[d] % CH_3CO	EtOH + HCl[e] % Alcoholysis	EtOH + HCl[e] % CH_3CO
Acetyl-*n*-valerylmethane	27	50	...	..	100	53	100	61
Acetyl-isovalerylmethane	19	65	...	..	85	58	20–30	65
Acetyl-trimethylacetylmethane	26 (250°)	90	...	..	65	75	20–30	91
Acetylcyclohexanoylmethane	..	...	...	..	100	53	100	58
Acetylbenzoylmethane	43	100	100	80	100	80	100	100
Dibenzoylmethane	58	...	...	..	100	..	0	...
	9 (150°)		34 (150°)					
Diacetylmethane	13	...	100	..	...	..	100	...
	25 (250°)							

[a] The experimental conditions for alcoholysis unless noted otherwise were as follows: 37.5 and 187.5 millimoles of diketone and ethanol, respectively, 200°, eight hours and 120 ± 30 atmospheres' pressure. [b] The ethanol was dried twice over lime. [c] The ethanol was dried over lime and aluminum ethoxide. [d] The ethanol contained 0.2% aluminum ethoxide. [e] These data were previously reported by Kutz and Adkins for alcoholysis at 60° for 100–150 hours.

The outstanding facts that emerge from these data are:

(1) Alcohol which has been dried with aluminum ethoxide was quite inactive for the alcoholysis of 1,3-diketones. For example, diacetylmethane was cleaved to the extent of only 25% after eight hours at 250°.

(2) Alcohol which contained the few tenths of one per cent. of water which was not removed by drying it twice with a good quality of lime was a rather active reagent for the cleavage of 1,3-diketones. For example, diacetylmethane was 100% cleaved after eight hours at 200° when this moist ethanol was used. This fact taken in conjunction with the inactivity of ethanol dried over aluminum ethoxide renders it open to question whether ethanol completely free of water would react at all with diketones.

(3) Aluminum ethoxide was a very active catalyst for the alcoholysis of 1,3-diketones. For example, the amount of alcoholysis, of acetylisovaleryl-

methane was more than four times as great for a given length of time in the presence of aluminum ethoxide as it was in dry ethanol.

(4) Dibenzoylmethane which was resistant to alcoholysis in the presence of hydrogen chloride at 60° and atmospheric pressure was readily cleaved at 200° either with dry ethanol or ethanol containing aluminum ethoxide. In fact the order of rate of cleavage of dibenzoyl-, acetylbenzoyl- and diacetylmethane in dry ethanol at 200° is the reverse of that previously found for the relative rates of cleavage of the three diketones at 60° in ethanol containing hydrogen chloride.

(5) Branching of the chain adjacent to one carbonyl group decreased the rate of alcoholysis with dry ethanol just as it did with ethanol containing hydrogen chloride.

(6) The ratio of the products formed in the cleavage of an unsymmetrical 1,3-diketone was a function of the experimental conditions under which alcoholysis occurred. For example, acetylbenzoylmethane which gave only ethyl acetate and acetophenone when it was cleaved with dry ethanol or with ethanol and hydrogen chloride gave a 20% yield of ethyl benzoate and acetone when it was cleaved with moist ethanol or with ethanol containing aluminum ethoxide. In every case the acetyl cleavage was less with dry ethanol and with ethanol containing aluminum ethoxide than it was with ethanol and hydrogen chloride.

Alcoholysis of β-Keto Esters.—A study of the alcoholysis of β-keto esters is considerably more complicated than is one of the 1,3-diketones. This results from the greater stability of the keto esters and from the fact that such a keto ester may undergo condensation to compounds of the dehydroacetic acid type as well as cleavage. The cleavage reactions with water and ethanol are formulated as

$$CH_3COCH_2CO_2C_2H_5 + C_2H_5OH = 2CH_3CO_2C_2H_5 \quad (IV)$$

$$CH_3COCH_2CO_2C_2H_5 + H_2O = CH_3COCH_3 + C_2H_5OH + CO_2 \quad (V)$$

There is recorded in Table II a summary of experimental results obtained in subjecting various β-keto esters to the action of ethanol and butanol.

The data in Table II show clearly certain facts in regard to the alcoholysis of β-keto esters.

(1) Ethanol which has been dried over aluminum ethoxide was not an active reagent for the cleavage of β-keto esters. For example, from 51 to 68% of benzoylacetic, benzylacetoacetic and acetoacetic esters were recovered from a reaction mixture after eight to nine hours at 250°, while the remainder had chiefly undergone hydrolysis and condensation.

(2) Ethanol dried twice over lime and so containing a few tenths of one per cent. of water was an active reagent and brought about almost identically the same amount of reaction IV (acetone) as of reaction V (ethyl acetate), although of course twice as many moles of ethyl acetate as of acetone were produced.

TABLE II

ALCOHOLYSIS OF β-KETO ESTERS

Ester		Reagent		Time,	Temp.,	Hydrolysis,	Alcoholysis,	Condensation,	Unreacted,	Loss, %	
Name	m. mole	name[a]	m. mole	hrs.	°C.	%	%	%	%	Mechanical	Unknown
Acetoacetic	385	EtOH[c]	955	3	200	19	1	6	63	5	6
Acetoacetic	385	EtOH[c]	1915	21	200	37	1	4	53	3	2
Acetoacetic	385	EtOH[d]	1915	8	200	8	4	4	71	6	7
Acetoacetic	577	EtOH[d]	2885	12	250	18	51	23	0	3	5
Acetoacetic	310	EtOH[c]	1540	8	250	42	43	0	0	17	0
Acetoacetic	577	EtOH[b]	2885	8	250	15	2	5	68	7	3
Acetoacetic	385	EtOH[d]	385	8	250	10	39	20	0	15	16
Acetoacetic	385	n-C_4H_9OH	1095	8	200	2	1	0	81	10	6
Acetoacetic	385	n-C_4H_9OH	810	8	250	7	56	15	0	8	14
Monomethylacetoacetic	174	EtOH[d]	870	8	250	6	57	21	0	8	8
Dimethylacetoacetic	158	EtOH[d]	790	8	250	0	12	4	72	12	0
Benzylacetoacetic	100	EtOH[d]	500	10	250	13	72	14	0	1	0
Benzylacetoacetic	100	EtOH[b]	500	9	250	24	19	0	51	5	1
Benzoylacetic	200	EtOH[d]	1000	8	250	36	47	16	0	3	0
Benzoylacetic	83	EtOH[b]	633	9	250	29	2	0	64	5	0
Malonic	319	EtOH[d]	1545	8	250	..	20	9	61	8	2

[a] Terms in this column have the same significance as in Table I. It should be noted that the hydrogen introduced into the bomb was moist, and when it was allowed to escape through dehydrite the latter gained 0.86 g. in weight.

(3) Aluminum ethoxide was an active catalyst for alcoholysis. Since by its presence it reduces, if it does not eliminate, water from the sphere of reaction, there occurs little hydrolysis of the keto ester.

(4) Acetoacetic ester did not undergo alcoholysis at all readily at 200° even with moist alcohol, so that a temperature of 250° was required for the ready cleavage of the keto ester.

(5) n-Butanol was a more effective reagent for the alcoholysis of acetoacetic ester than was ethanol, apparently because butanol was more easily and more completely dried.

(6) Dimethylacetoacetic ester was found to be more resistant to alcoholysis than was the parent keto ester, there being only 12% cleavage after eight hours at 250°.

(7) The two monosubstituted (methyl and benzyl) acetoacetic esters underwent alcoholysis at least as readily as the parent ester, giving good yields of the esters of acetic and propionic, and of acetic and β-phenylpropionic acids, respectively.

(8) Benzoylacetic ester even in the presence of aluminum ethoxide gave a high percentage of hydrolysis to acetophenone as well as alcoholysis to ethyl acetate and benzoate.

Hydrolysis of 1,3-Diketones and β-Keto Esters.—There is recorded in Table III a summary of the data obtained in subjecting various keto esters and acetylbenzoylmethane to hydrolysis. The important con-

clusions that may be drawn from the data in Table III would appear to be:

(1) The method of cleaving β-keto esters with water or with water containing a base at 200° gave excellent yields of the corresponding ketones, with little or no acid formation. Meerwein[4] subjected certain β-keto esters to hydrolysis at 200° in a sealed glass tube. He obtained a 73% yield of acetophenone from benzoylacetic ester, an 88% yield of 4-phenylbutanone-2 from α-benzylacetoacetic ester and unstated amounts of ketones from five other esters which were reported as completely hydrolyzed.

TABLE III

HYDROLYSIS OF β-KETO ESTERS AND 1,3-DIKETONES

Compound		Reagents				
Name	Millimoles	Name	Millimoles	Time, hrs.	Temp., °C.	Yield (%) of product(s)
Acetoacetic ester	385	Water	1945	9[b]	200	97% acetone
Benzylacetoacetic ester	114	Water	1390	8[b]	200	97% 4-phenylbutanone-2
Diethylacetoacetic ester	168	EtOH[a]	860	11	250	No cleavage
		Water	514			
Dimethylacetoacetic ester	160	Water	1600	12	250	50% Me-butanone-3
Dimethylacetoacetic ester	160	NaOH	200	10[b]	250	5% acetic and isobutyric acids;
		Water	5000			70% 2-Me-butanone-3
Diethylacetoacetic ester	310	EtOH	850	8	200	49% 3-Et-pentanone-2; 45%
		Water	2780			diethylacetoacetic ester
		NaOH	375			
Diethylacetoacetic ester	200	EtOH	1700	8	250	84%[d] 3-Et-pentanone-2; no
		Water	2780			residual ester
		NaOH	240			
Ethyl trimethylacetate	232	Water	2320	8	200	36% hydrolysis of ester
Ethyl α,α-diethyl-β-hydroxybutyrate	53	Water	1060	8	250	No hydrolysis
Acetylbenzoylmethane	37.5	Water[c]	188	8	200	76% acetic acid; 24% benzoic acid

[a] Ethanol used as a solvent to ensure contact of reactants. [b] The time intervals are no doubt much longer than necessary for complete reaction as 385 m. moles of acetoacetic ester was completely hydrolyzed by 400 m. moles of water within one hour at 200°. [c] Cleavage was not complete after eight hours at 200°, so 555 m. moles of water was added and the mixture kept at 250° for five and one-half hours. [d] The amount of ethanol used rendered the isolation of the ketone more difficult and probably materially reduced the yield of ketone obtained.

(2) The dimethyl- and diethylacetoacetic esters were quite resistant to hydrolysis even at 250°. The diethyl ester showed no trace of hydrolysis after repeated attempts at 250°. This resistance to hydrolysis of trisubstituted acetic acids is not limited to keto esters but was also manifested by trimethylacetic ester and especially by α,α-diethyl-β-hydroxybutyric ester, which showed no hydrolysis after eight hours at 250°. The inactivity of these esters would appear to be the result of steric hindrance. The resistance to hydrolysis at atmospheric pressure of the dialkylacetoacetic esters, especially those containing alkyl groups larger than methyl, was observed by Michael[5] and utilized by him in purifying dialkylacetoacetic esters.

[4] Meerwein, *Ann.*, **398**, 242 (1913).

[5] Michael, *Ber.*, **38**, 2083 (1905).

(3) The ratio of cleavage products in the hydrolysis of acetylbenzoylmethane with water at 250° was similar to that obtained with moist ethanol.

Experimental Part

All of the experiments on the alcoholysis of diketones and keto esters reported in this paper were carried out in the apparatus recently described[6] in glass or copper containers under a pressure of 90–150 atmospheres of hydrogen. The diketones were from the same preparation as those used by Kutz and the reaction products, with the exceptions noted below, were analyzed as described by him.[7] The exceptions were made in that no phenylhydrazine was used if alcoholysis was complete as evidenced by a test with ferric chloride, and in that 2,4-dinitrophenylhydrazine and benzyl alcohol were used instead of phenylhydrazine and butanol in the determination of the extent of cleavage of dibenzoylmethane.

The method of analysis of the reaction products of the alcoholysis of β-keto esters and the calculation of the yields is best presented in describing a specific experiment. Seventy-five grams (0.58 mole) of acetoacetic ester and 132.7 g. (2.88 moles) of ethanol containing 0.26 g. of aluminum ethoxide were heated for twelve hours at 250°. The reaction products after removal from the bomb weighed 197.5 g. The loss (10.2 g.) was in part mechanical and in part due to the escape of carbon dioxide. The latter was identified by bubbling the gas from the bomb through a solution of barium chloride. The bomb and liner were washed out with ethanol and the combined liquid reaction products (which showed no enol test) distilled through a Widmer column having a spiral 25 cm. in length. All except 17.0 g. distilled below 79°. The mixture of acetone, ethanol and ethyl acetate was then analyzed for acetone by the sodium sulfite method[8] and for the ester by saponification. The acid used in the analysis for acetone had been standardized against solutions of acetone containing ethanol and ethyl acetate.[9] These analyses showed 5.86 g. of acetone (0.101 mole) and 51.9 g. of ethyl acetate (0.59 mole). The ketone was identified by the preparation of its 2,4-dinitrophenylhydrazone (m. p. 127–128°) and the determination of a mixed melting point (126–128°) with an authentic sample of the hydrazone of acetone. The percentages of hydrolysis and alcoholysis were calculated on the basis of equations IV and V directly from the amounts of acetone and ethyl acetate as found by analysis. The percentage conversion of acetoacetic ester to condensation products of b. p. above 45° (16 mm.) was calculated on the basis of its weight (17.0 g.) and the assumption that it was molecularly equivalent to acetoacetic ester. The amount of carbon dioxide (equation V) was calculated from the amount of acetone found and deducted from the 10 g. loss found on opening the bomb. This reduced the mechanical loss to 3% and left 5% of the acetoacetic ester unaccounted for.

This procedure for the study of the products from the alcoholysis was modified in some experiments as noted below. (1) If any unchanged keto ester remained after alcoholysis it was separated from the other products by fractionation. (2) Duclaux values were obtained upon the acids from the alcoholysis of α-methyl acetoacetic

[6] Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930); see also *Ind. Eng. Chem., Anal. Ed.*, **4**, 342 (1932).

[7] Kutz and Adkins, *ibid.*, **52**, 4036 (1930).

[8] Child and Adkins, *ibid.*, **45**, 3013 (1923).

[9] *Cf.* Adkins, Semb and Bolander, *ibid.*, **53**, 1853 (1931).

ester and indicated that both propionic and acetic acids were formed. (3) The alcoholysis of α-benzylacetoacetic ester gave ethyl acetate, ethyl β-phenylpropionate and 4-phenylbutanone-2. The ethyl acetate was obtained as in the alcoholysis of acetoacetic ester but the higher boiling ester and the ketone were obtained in a fraction 104–105 (9 mm.). In general the ester was determined by saponification and the ketone by difference. In one run the analytical procedure was checked by the isolation of the ketone. (4) The alcoholysis of benzoylacetic ester also gives a mixture of esters and ketone which were determined as in the case of α-benzylacetoacetic ester, except that in this case the mixture of ester and ketone boiled at 90–95° (12 mm.).

The acetone and acetic acid obtained by the hydrolysis of acetoacetic ester were determined by titration. 4-Phenylbutanone-2 resulting from the hydrolysis of α-benzylacetoacetic ester was extracted with ether, dried over potassium carbonate and 16.4 g. distilled at 110.5–111° (13 mm.). Ethyl α,α-diethylacetoacetate after attempted hydrolysis was recovered unchanged to the extent of 95.3%.

The products from the hydrolysis of α,α-dimethylacetoacetic ester (25.5 g.) were extracted with ether, dried over sodium sulfate and fractionated. After the removal of the solvent the following fractions were obtained: (1) 75–85°, 5.3 g.; (2) 85–169° 1.9 g.; (3) 169–181° (mostly 170–179°) 9.3 g.; (4) residue, 4.2 g. A good yield of a semicarbazone of m. p. 111–112° was obtained from fraction 1; this corresponds with the melting point (112°) of the semicarbazone of methyl isopropyl ketone. The above figures indicate that approximately one-half of the keto ester was hydrolyzed to the ketone with no evidence for the formation of acids.

The product from the alkaline hydrolysis of α,α-dimethylacetoacetic ester was acidified with sulfuric acid, heated on a steam-bath to complete the expulsion of carbon dioxide, extracted with ether, dried over sodium sulfate and fractionated. Fraction (1) 35–75°, 1.96 g.; (2) 75–85°, 5.49 g.; (3) 85–93° (mostly 91–93°) 4.40 g.; (4) residue, 2.57 g. The residue was no more than the normal amount of liquid held back by the fractionating column and flask used. It contained 0.015 mole of acid. It thus appears that all except approximately 5% of the keto ester was converted to the ketone. The procedure in working up the product from the alkaline hydrolysis of diethylacetoacetic ester was essentially the same as that just described.

Summary

The alcoholysis and hydrolysis of a number of 1,3-diketones and β-keto esters at 150–250° under pressures in the vicinity of 100 atmospheres have been investigated. Ethanol which had been dried over aluminum ethoxide was found to be a rather inactive reagent for the alcoholysis of 1,3-diketones and β-keto esters, while ethanol containing a few tenths of one per cent. of water was a very much more active reagent. Aluminum ethoxide was found to be quite an active catalyst for alcoholysis. The keto esters were much more resistant to alcoholysis than were the diketones, the reaction of the latter proceeding approximately as rapidly at 150° as did the alcoholysis of the keto esters at 250°. α-Methyl- and α-benzylacetoacetic esters underwent alcoholysis approximately as rapidly as did the parent ester, while the dimethyl and diethylacetoacetic esters were very resistant to cleavage. Excellent yields of ketones were obtained by the hydrolysis at 200° of several β-keto esters. Dialkyl substituted β-keto esters were quite stable toward water at 200° so that they may be freed of

monoalkyl substituted β-keto esters by such a treatment. The hydrolysis of these dialkyl β-keto esters necessitates the use of alkali at 250°. The ratio of the products formed in the cleavage of unsymmetrical 1,3-diketones varied greatly with variation in the environment during cleavage.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE USE OF KETENE IN THE PREPARATION OF SIMPLE AND MIXED ACID ANHYDRIDES

BY CHARLES D. HURD AND MALCOLM F. DULL

RECEIVED MAY 13, 1932 PUBLISHED AUGUST 5, 1932

Mixed acid anhydrides, R—CO—O—CO—CH_3, are generally made[1] either by refluxing the acid, RCOOH, with acetic anhydride or by the interaction[2] of any acyl chloride and sodium acetate or by reaction of the acid with acetyl chloride and pyridine. A purification procedure is essential in all of these cases. Such anhydrides as acetic propionic anhydride or acetic isovaleric anhydride are sufficiently stable to be distilled under diminished pressure, but the tendency of mixed anhydrides to disproportionate into the two symmetrical anhydrides often makes the isolation of the mixed anhydride difficult or impossible.

Ketene is an acetylating agent but it has never been considered for use in preparing mixed acetic anhydrides. Ketenes which have been added to acids to convert them into mixed anhydrides are diphenylketene and carbon suboxide.[3] Van Alphen's is the only account[4] of the reaction of ketene itself with acids. He used phenolic acids and observed acetylation of the phenolic group. No mention was made of the production of mixed anhydrides.

In the present work it has been found that ketene readily attaches itself to aliphatic or aromatic acids giving rise to mixed acetic anhydrides

$$RCOOH + CH_2{=}C{=}O \longrightarrow RCO{-}O{-}COCH_3$$

Since nothing else is formed, the purification procedure is greatly simplified. Thus, using ketene, acetic acid was quantitatively changed into acetic anhydride, *n*-butyric acid into acetic butyric anhydride, benzoic acid into acetic benzoic anhydride and furoic acid into acetic furoic anhydride.

Distillation of acetic benzoic anhydride or of acetic furoic anhydride, both of which were oils, gave rise to benzoic anhydride and furoic anhydride,

[1] Autenrieth, *Ber.*, **20,** 3187 (1887); **34,** 168 (1901); Béhal, *Ann. chim. phys.*, [7] **19,** 274 (1900); **20,** 418 (1900); Autenrieth and Thomae, *Ber.*, **57,** 423 (1924).

[2] Verkade, *Rec. trav. chim.*, **35,** 299 (1915); Kilpatrick and Kilpatrick, THIS JOURNAL, **52,** 1418 (1930).

[3] Staudinger, *Ann.*, **356,** 79 (1907); Diels and Lalin, *Ber.*, **41,** 3426 (1908).

[4] Van Alphen, *Rec. trav. chim.*, **44,** 838 (1928).

both solids, in excellent yields. Disproportionation was evident also with acetic butyric anhydride. Thus, this use of ketene serves to produce not only mixed acetic anhydrides, but also symmetrical acid anhydrides by pyrolysis of the mixed anhydrides. The reaction should be a perfectly general one for acids which possess no interfering groups such as hydroxyl or amino.

With aniline, acetic benzoic anhydride is converted into benzoic acid and acetanilide

$$C_6H_5CO{-}O{-}COCH_3 + C_6H_5NH_2 \longrightarrow C_6H_5COOH + C_6H_5NHCOCH_3$$

and not into acetic acid and benzanilide. This agrees with Béhal's finding that ammonia reacted with the mixed anhydride to give benzoic acid and acetamide almost exclusively. If the mixed anhydride was left for twenty-four hours before adding the aniline, both of the anilides and both acids were formed indicating the gradual transformation of the mixed anhydride into benzoic anhydride and acetic anhydride.

Acetic furoic anhydride behaved analogously in its reaction with aniline. The only anilide formed was acetanilide. In the case of acetic butyric anhydride, both anilides were produced but the yield of butyranilide exceeded that of acetanilide.

This behavior of aniline toward the mixed acetic anhydrides is predictable on the basis of the generally recognized greater electron attraction of aryl radicals than alkyl and the slightly greater attraction of methyl than *n*-propyl inasmuch as the molecule of the mixed anhydride is entirely symmetrical except for the terminal groups. The electronic configuration for benzoic acetic anhydride which expresses these factors is

$$C_6H_5{:}\ \underset{O}{C}{:}\ \ddot{O}{:}\ \underset{O}{C}{:}\ CH_3$$

That the absorption of ketene by acids is not limited to organic acids was demonstrated by a few preliminary experiments with sulfuric and phosphoric acids. Ketene was quantitatively absorbed, presumably with the formation of acetylsulfuric acid and acetylphosphoric acid. The utility of the method with other inorganic acids, for example, in the synthesis of acetyl nitrate, is also evident.

Experimental Part

Ketene was prepared from acetone[5] by pyrolysis. Instead of distilling the acetone into the reaction tube it was dropped in directly from a separatory funnel. In this way, such a rapid flow of acetone was maintained that the extent of decomposition at 700° was limited to 5–6%. Thus, from 108 g. of acetone 102 g. was recovered in an experiment lasting thirty minutes. The other 6 g. gave rise to a 72% yield of ketene since 10 g. of acetanilide was produced from it (*via* aniline + ketene).

Acetic Acid[6] and Ketene.—Slightly more than the theoretical quantity of ketene

[5] Hurd, "Organic Syntheses," John Wiley and Sons, New York, 1924, Vol. IV, p. 40.

[6] Compare Hurd and Martin, THIS JOURNAL, **51**, 3614 (1929).

was bubbled into acetic acid. From 20 cc. of this which was distilled, 17 cc. was collected between 136–138°. Thus, the conversion of acetic acid into acetic anhydride is nearly quantitative.

n-**Butyric Acid and Ketene.**—Two grams of butyric acid (b. p. 161–163°) was treated with the calculated quantity of ketene. Any admixed acetone was evaporated off *in vacuo* and the residual acetic butyric anhydride was analyzed. Whitford's method of analysis[7], which was developed for acetic anhydride, was found to apply with the mixed acetic anhydride. In it, the anhydride reacts with dry oxalic acid and pyridine to liberate carbon monoxide and carbon dioxide which are collected.

Anal. Subs., 0.2166, 0.2112; calcd. cc. of gas for $CH_3COOCOC_3H_7$, 72.9, 72.7; found, cc., 72.0, 72.1; per cent. of $C_6H_{10}O_3$, 98.7, 99.1.

The acetic butyric anhydride was found to boil[8] at 147–160°, above which the boiling point rose abruptly to that of butyric anhydride itself. At 18 mm. the mixed anhydride boiled at 70–85°. With aniline it reacted vigorously, yielding butyranilide and a smaller quantity of acetanilide. The butyranilide crystallized first and was removed but the acetanilide crystallized almost immediately thereafter. After recrystallization from water the former melted at 89–90° and the latter at 110–112°.

Inasmuch as there was no sharp boiling fraction for the mixed anhydride in the above experiment, it was repeated on a larger scale. Twenty grams of redistilled *n*-butyric acid (b. p. 161–162°) was treated with ketene until addition of anhydrous sodium carbonate failed to result in an evolution of carbon dioxide. The crude product was allowed to stand over anhydrous sodium carbonate for two hours, after which the excess solvent (anhydrous ether and some acetone which had carried over) was removed by evacuating for half an hour with a water pump. A portion, treated with aniline, resulted in the formation of both acetanilide and butyranilide, the latter predominating.

The crude material (30 g.) was then fractionated at 7 mm. pressure. The first fraction of 15.5 g. was collected at 41–60°, the second of 10.5 g. at 60–66°, and the third of about 3 g. at 66–67°. The third fraction was butyric anhydride, for it yielded only butyranilide on treatment with aniline. The first fraction produced acetanilide and butyranilide with acetanilide in excess. The fraction was evidently a mixture of acetic anhydride and acetic butyric anhydride. Redistillation of this fraction failed to produce a constant boiling fraction. It distilled at 41–62°.

The second fraction (10.5 g.) gave rise to both butyranilide and acetanilide with the latter in considerably smaller amounts. On redistillation, it came over almost entirely at 63–64.5°. A fraction was thus obtained weighing 9.5 g. which, with aniline, again yielded both butyranilide and acetanilide. Much of both anilides was lost in the steps of purification but it was certain that more butyranilide was obtained than acetanilide.

Benzoic Acid.—(a) Ketene was passed through a tower which contained powdered benzoic acid. Some ketene escaped but some reacted as witnessed by a heat of reaction and by a gradual liquefaction of the solid acid into the liquid benzoic acetic anhydride. Accumulation of this mixed anhydride was slow by this method. Furthermore, the heat of reaction seemed to cause a partial disproportionation into benzoic anhydride.

(b) Using ether as a solvent, the reaction was more rapid and the temperature was kept under control. Ketene was passed into a solution of twenty grams of benzoic acid in 100 cc. of ether. To follow the reaction a stirring rod was dipped occasionally into the solution and withdrawn. Evaporation of the solvent left a solid at the start

[7] Whitford, THIS JOURNAL, **47**, 2939 (1925).

[8] Autenrieth, *Ber.*, **34**, 177 (1901), gave 155–175° as the b. p.

but only an oil at the conclusion of the reaction. After evaporation of the ether, 31–32 g. of benzoic acetic anhydride remained which is a quantitative yield.

Identification of Benzoic Acetic Anhydride

(a) **Analysis,** using dry oxalic acid and pyridine.

Anal. Subs. 0.2131, 0.2213; calcd. cc. of gas for $CH_3COOCOC_6H_5$, 58.2, 60.4; found, cc., 57.5, 59.3; per cent. of $C_9H_8O_3$, 98.8, 98.2.

(b) **Disproportionation to Benzoic Anhydride.**—The 31.5 g. of oil was distilled at 18 mm., giving 13 g. of acetic anhydride (collected below 210°) and 18.5 g. of benzoic anhydride which boiled at 210–210.5°. The latter solidified and melted at 41.5°. The 18.5 g. represents a 96% yield of benzoic anhydride.

In another run, two 25-g. portions of benzoic acid (each in 125 cc. of ether at room temperature) were connected in series to a stream of ketene. (The two were interchanged when the first portion was nearly converted.) In this run the acetone was dropped in the furnace at a rate of 4.5 cc. per minute. The time for the entire 50 g. to be changed to the mixed anhydride was 135 minutes. Distillation of the mixed anhydride gave 42 g. of benzoic anhydride (m. p. 42°) or a 93% yield.

(c) **Reaction with Aniline.**—To 10 g. of benzoic acetic anhydride (similar preparation from another experiment), 5.5 g. of aniline was added. Much heat was evolved and on cooling the mass solidified. By extraction with diluted sodium carbonate and subsequent acidification 6.5 g. of benzoic acid was obtained as compared with a theoretical yield of 7.4 g. The residue of acetanilide was dissolved in boiling water, whereupon 6.8 g. (calcd. is 8.2 g.) precipitated after filtering and cooling. About 0.3 g. of benzanilide, m. p. 163°, resisted solution in the water.

If the 10 g. of mixed anhydride was left for twenty-four hours before mixing it with aniline, there was considerable disproportionation as evidenced by the formation of 3.3 g. of benzoic acid, 4.1 g. of acetanilide and 4.2 g. of benzanilide.

Furoic Acid.—Ketene was passed into a solution of 25 g. of furoic acid in 150 cc. of ordinary ether. The details of this reaction were similar to those given with benzoic acid in ether solution. This run was completed in seventy-five minutes. On evaporation of the solvents, an oil remained which was furoic acetic anhydride. The yield was quantitative.

Anal. Subs. 0.1987, 0.2016: calcd. cc. of gas for $CH_3COOCOC_4H_3O$, 57.8, 58.6; found, cc., 56.7, 57.1. Per cent. of $C_7H_6O_4$, 98.1, 97.4.

Reaction with Aniline.—The mixed anhydride reacted vigorously with aniline. The exclusive products of the reaction were acetanilide (m. p. 113–114°) and furoic acid (m. p. 129–131°) which were separated and purified by crystallization from water.

Vacuum Distillation of Furoic Acetic Anhydride.—The mixed anhydride from 10 g. of furoic acid was distilled at 5 mm. Eleven grams of an almost odorless distillate was collected at 109–110°, and 2.7 g. at 150–152°. The latter quickly solidified (m. p. 71°) and was identified as furoic anhydride.[9] The eleven grams of liquid distillate was largely unchanged furoic acetic anhydride. Considerable disproportionation of the mixed anhydride occurred when the distillation was performed at 22 mm., the furoic anhydride distilling at 196–197°. Using atmospheric pressure for the distillation, there was complete and rapid pyrolysis to the symmetrical anhydrides.

Summary

Mixed acetic anhydrides, RCO—O—$COCH_3$, may be prepared very smoothly by interaction of ketene with acids. The mixed anhydrides

[9] Baum, *Ber.*, **34**, 2505 (1901).

were analyzed, using dry oxalic acid and pyridine. The reaction with aniline was investigated. The disproportionation induced by heat was found to be a convenient method for synthesizing symmetrical acid anhydrides.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY AND OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

NEOPENTYL ALCOHOL AND ITS REARRANGEMENT PRODUCTS[1]

BY FRANK C. WHITMORE AND HENRY S. ROTHROCK[2]

RECEIVED MAY 17, 1932 PUBLISHED AUGUST 5, 1932

The literature on neopentyl alcohol (*tert.*-butylcarbinol) and the related halides[3] is unsatisfactorily incomplete, especially in view of the fact that these substances represent the simplest case in which removal of the alcoholic hydroxyl results in complete or nearly complete rearrangement of the carbon skeleton.[4]

The present study fills some of the gaps in our knowledge of this interesting group of substances. Neopentyl alcohol is stable to heat. Seven weeks at 230–240° gives no change. Heating to similar temperatures with iodine, anhydrous potassium carbonate or traces of hydrogen chloride gives little or no change. It dissolves in cold concentrated sulfuric acid with the formation of an acid ester from which the original alcohol can be recovered.

The preparation of halides from neopentyl alcohol is extraordinarily difficult. Its reactivity is much less than that of *n*-butyl alcohol. Dry hydrogen bromide very slowly forms an oxonium salt with neopentyl alcohol. This is stable at 40° but is slowly converted at 65° to a mixture of amyl bromides containing approximately 72% tertiary amyl bromide, 8% of a secondary bromide, probably secondary isoamyl bromide and 20% of one or more primary bromides. The composition of this mixture is not changed by heating at 105°.

The problem of the neopentyl halides and their rearrangements is being intensively studied in this Laboratory.

Experimental

The neopentyl alcohol used in this research was prepared from *tert.*-butylmagnesium chloride and formaldehyde by R. W. Beattie, of the Intermediate Laboratory of the Public Health Institute of Chicago.

Stability of Neopentyl Alcohol on Heating.—The relatively high melting point of

---

[1] Submitted by Henry S. Rothrock in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Du Pont Fellow, Northwestern University, 1928–1929.

[3] Tissier, *Ann. chim. phys.*, [6] **29**, 357 (1893); Samec, *Ann.*, **351**, 256 (1907); Richard, *Ann. chim. phys.*, [8] **21**, 323 (1910); Ingold, *J. Chem. Soc.*, **123**, 1706 (1923).

[4] See p. 3279.

the alcohol (52°) was used in detecting any change due to the action of heat or reagents. This method was rendered more delicate by the large freezing point constant of the alcohol. This was found to be 11.0 ± 0.2 as compared with 5.1 for benzene and 1.86 for water. Thus 5% of water in the alcohol renders it liquid at room temperature.

A sample of neopentyl alcohol of m. p. 50° was sealed in a Pyrex tube filled with carbon dioxide, and heated at 230–240° for fifteen hours. The tube was then cooled and the melting point determined without opening the tube. The m. p. was 44–46°. The heating at 230–240° was then continued for forty-eight days, at the end of which time the m. p. was still 44–46°.

The Action of Reagents with Neopentyl Alcohol

(*a*) **Iodine.**—A sample of the alcohol (m. p. 50°) was sealed in a Pyrex tube with a crystal of iodine and heated at 230–240° for fifteen hours. A slight charring occurred and the m. p. dropped to 41–43°. After heating again for forty-eight days the m. p. was still 41–43°.

(*b*) **Anhydrous Potassium Carbonate.**—A sample of alcohol (m. p. 52°) was heated in a sealed tube with an equal weight of freshly dehydrated potassium carbonate at 225° for ten hours. The m. p. was 49°. After heating again for seven days at 225° the m. p. was 48–49°.

(*c*) **Traces of Hydrogen Chloride.**—Approximately 5 cc. of dry hydrogen chloride gas was passed into 4.5 g. of neopentyl alcohol (m. p. 51°) in a Pyrex tube. The tube was sealed and heated for thirty-four hours at 175°. The m. p. was 43–45°. The material was slightly pink. The tube was heated for two days more at 175°, three days at 200° and finally two weeks at 200° without any further change in the m. p. after each of these periods.

(*d*) **Cold Concentrated Sulfuric Acid.**—A mixture of 5 g. of neopentyl alcohol (m. p. 50°) and 5 cc. of C. P. sulfuric acid was prepared at 0°. About ten minutes' shaking was required to effect complete solution. The mixture was poured on 50 g. of finely ground ice. After the ice had melted, the solution was made barely alkaline with 25% sodium hydroxide solution and saturated with solid potassium carbonate. An upper layer (2 g.) separated which was neopentyl alcohol, m. p. 40–42°. The aqueous layer was extracted with ether, the ether solution dried with potassium carbonate and the ether removed by distillation. The residue reacted with phenyl isocyanate to give 3 g. of the phenyl urethan of neopentyl alcohol, m. p. 108–110°. This corresponded to 1.5 g. of the alcohol. Since the above experiment was carried out in such a way as to avoid mechanical loss of the alcohol and yet only 3.5 g. was recovered of the 5 g. used, it appeared that some other product was formed. This proved to be a stable acid ester of the alcohol, according to the following experiment.

A solution of neopentyl alcohol in C. P. sulfuric acid was allowed to stand at 20°. The solution first turned red and began to deposit crystals after twenty-four hours. After six days the entire mass was solid with crystals. The crystals were soluble in water, alcohol, benzene and ether. When the crystals were refluxed with water and steam distilled, neopentyl alcohol was recovered and identified as the phenyl urethan, m. p. 110–111°. Attempts to make a crystalline barium salt of the acid ester failed.[5] Treatment of tertiary amyl alcohol with sulfuric acid under the same conditions gave only a red viscous liquid from which the alcohol was recovered on dilution.

Formation of Halides from Neopentyl Alcohol

1. Action of Hydrogen Chloride.—All attempts to repeat the work of Tissier and of Richard[3] failed to give any chloride. Only one experiment will be described. Twenty-eight grams of neopentyl alcohol in a tube cooled to −10° was saturated with dry

[5] *Cf.* Tissier, *Compt. rend.*, **112**, 1065 (1891).

hydrogen chloride gas and sealed. The tube was heated for 206 hours at 62–65°. The contents turned deep red-brown. Only one layer was present at any time. When the tube was cooled and opened, a violent evolution of hydrogen chloride occurred. The contents of the tube dissolved completely in 100 cc. of concentrated hydrochloric acid, indicating the absence of appreciable amounts of chlorides. Extraction with ether gave 10 g. of unchanged neopentyl alcohol. No trace of chloride was detected.

2. Action of Thionyl Chloride.—The method of Darzens,[6] modified until it gave over 30% yields of *n*-butyl chloride from *n*-butyl alcohol, was applied to neopentyl alcohol. Twenty grams of neopentyl alcohol, 21 g. of dry pyridine and 22 cc. of dry ether were placed in a flask provided with a stirrer and a dropping funnel. The mixture was cooled to 0° and a solution of 29 g. of thionyl chloride in 27 cc. of dry ether was added slowly with vigorous stirring and cooling. After twenty-four hours the mixture was worked up in the usual way. This gave 16 g. of neopentyl alcohol, b. p. 108–112°, m. p. 41–43°, but no detectable chloride.

3. Action of Phosphorus Tribromide.—Twenty-nine grams of neopentyl alcohol, cooled to 0°, was treated slowly with 30 g. of phosphorus tribromide. After standing at room temperature for eight days, the mixture was poured into a large volume of ice water. A layer lighter than water separated. Most of this was unchanged alcohol, as shown by its solubility in concd. sulfuric acid. The total yield of bromide was 7 g. or 14%. A similar experiment with *n*-butyl alcohol gave a 50% yield.

4. Action of 48% Hydrobromic Acid.—Twenty grams of neopentyl alcohol was treated with 150 cc. of 48% hydrobromic acid in an all-glass reflux apparatus. On heating to 50°, the mixture turned black. The mixture was refluxed for twenty-five minutes and allowed to stand overnight. It was then distilled. A fraction passed over at 78–90°. This separated into two layers. The lower layer was water and the upper layer was completely soluble in concd. sulfuric acid, showing the absence of organic bromides. *n*-Butyl alcohol in a similar experiment gave an 80% yield of the bromide.

5. Action of Dry Hydrogen Bromide.[7] (*a*) **At 40°.**—The work of Tissier[3] could not be repeated. Eleven grams of neopentyl alcohol was saturated at −10° with dry hydrogen bromide prepared from bromine and boiling tetralin and purified by red phosphorus and phosphorus pentoxide. Even after this mixture was heated at 40° in a sealed tube for weeks, no separation into layers occurred.

(*b*) **At 65°.**—Only one of several experiments will be described. This used 188 g. (2.1 moles) of neopentyl alcohol, m. p. 48–50°. When dry hydrogen bromide was passed over the alcohol, the temperature rose rapidly to 50°. Hydrogen bromide was then passed through the liquid and cooling was applied. When it was saturated at 10°, 69 g. of the calculated quantity of 172 g. of hydrogen bromide had been absorbed. The reaction flask was capped with a stopper carrying two toy balloons coated inside with liquid paraffin. After standing for eight days the pressure of hydrogen bromide had dropped although no separate layers had appeared. The mixture was again saturated with hydrogen bromide, this time at 4° with a gain in weight of 37 g. After one day at room temperature, the mixture was again saturated with hydrogen bromide, now at −5°, with a gain in weight of 34 g. At further intervals of six and thirteen days 27 g. and 10 g. of hydrogen bromide were added at −10°. It thus required twenty-eight days to introduce slightly more than the calculated amount of hydrogen bromide. No layers separated.

In order to determine whether or not a stable bromide had been formed, two weighed samples were treated as follows. (1) Dry nitrogen was passed through until no more

[6] Darzens, *Compt. rend.*, **152**, 1314, 1601 (1911).

[7] This work was checked and extended by P. A. Krueger, while working in this Laboratory, under a Grant-in-aid from the National Research Council.

hydrogen bromide was driven out. The loss in weight was 49%. The residue smelled like neopentyl alcohol but did not solidify at −20°. It gave a qualitative test for an organic bromide. (2) Shaking for ten minutes with cold water removed 43% of the weight of the mixture as hydrogen bromide, which was determined as silver bromide.

Seventy-eight grams of the mixture containing 40 g. of neopentyl alcohol and 38 g. of hydrogen bromide was sealed in a 300-cc. Pyrex tube and heated at 65°. After twenty days no visible change had occurred. It was opened and saturated with hydrogen bromide at −20°. After five days more at 65°, a few drops separated on top. After two days more, the tube was opened, saturated again at −20° and heated at 65°. Four days later the two layers were about equal in volume. The upper layer increased in volume for nine days more. The upper layer then consisted of 61.5 g. of bromides and the lower layer of 20.1 g. of concd. hydrobromic acid. It thus took forty days at 65° to complete the conversion to bromides.

The bromide layer lost only 1.7 g. when washed with 21.3 g. of 40% hydrobromic acid. It was dried for nineteen hours at 0° over anhydrous calcium bromide. It was then distilled at 23–25 mm. at 22–32°. About 90% distilled at 22–24° at this pressure. Only 1 cc. of residue was left. The distillate was water-white, of an organic bromide odor and free from hydrogen bromide, yield 53.0 g. A second tube treated in a similar way gave 47.5 g. of bromides distilling at 22–30° at 25 mm.

Anal. Calcd. for $C_5H_{11}Br$: Br, 52.9. Found: Br, 53.2.

Nature of the Halides from Neopentyl Alcohol

1. Freezing Point Studies.[8]—The measurements were made by means of a Leeds and Northrup Type K potentiometer and a chromel–copel thermocouple standardized at the freezing points of pure *n*-heptane (−90.7°) and pure 2,2,4-trimethylpentane (−107.7°). The distilled samples of the bromides from neopentyl alcohol froze from −94 to −104° at which point complete solidification prevented stirring. Check determinations were made repeatedly with both preparations. Most of the material froze at −94 to −99°. Since the neopentyl halides reported in the literature are said to rearrange on heating, a sample was heated for nine hours at 105°. A slight darkening occurred. The bromide was subjected to a pressure of 20 mm. for a few seconds to allow any hydrogen bromide or olefin to boil out. The freezing point was then found to be unchanged, showing that the proportion of various bromides in the mixture had not been changed by heating.

Tertiary amyl alcohol, b. p. 101–101.5° (735 mm.), was treated with constant boiling hydrobromic acid to form tertiary amyl bromide, b. p. 106.5–107° (735 mm.). This froze at −82 to −85°. Addition of tertiary amyl bromide to the bromides from neopentyl alcohol *raised* the m. p. about 2 and 7°, respectively, for the addition of 2 cc. and 5 cc. of the tertiary amyl bromide to 5-cc. portions of the bromides from neopentyl alcohol. It was found that an equimolar solution of pure tertiary amyl bromide and pure ethyl bromide froze about 30° lower than the tertiary amyl bromide. Since the bromides from neopentyl alcohol froze about 10° lower than the tertiary bromide and had their freezing points raised by the addition of the latter, they must contain tertiary amyl bromide with about one-third of a mole of isomeric bromides for each mole of the tertiary bromide. The isomeric bromides were not converted to tertiary bromide by heating at 105° for nine hours.

2. Analysis for Primary, Secondary and Tertiary Bromides.—The method of Michael and Zeidler[9] was used.

---

[8] The mixture was studied by means of freezing point measurements because of the supposed instability of the mixture and its tendency to rearrange during chemical reactions.[3,5]

[9] Michael and Zeidler, *Ann.*, **385**, 271 (1911).

(a) A weighed sample (about 0.2 g.) of the bromide was shaken vigorously for twenty-five minutes on a mechanical shaker with 10 cc. of distilled water. The solution was then analyzed by the Volhard method, carefully avoiding the presence of any appreciable excess of silver nitrate. In this way 38.2% of bromine was found. Thus 72% of the total bromine in the mixture was removed by hydrolysis with cold water in twenty-five minutes, indicating the presence of approximately that amount of tertiary halide. When an excess of the standard silver nitrate solution (about 0.1 *N*) was shaken with a sample of the bromide, an additional 4.2% of bromine was removed, thus indicating the presence of about 8% of secondary bromide in the mixture. The remaining 20% of bromide in the mixture is undoubtedly primary bromide and accounts for the nitrolic acid test for primary bromides obtained by Tissier.[3,5] The small amount of the mixture of secondary and primary bromides obtained distilled at 100–115° (secondary isoamyl bromide, b. p. 114°, *sec.*-butylcarbinyl bromide, b. p. 116–118°). Attempts to prepare a Grignard compound from the primary bromide failed. Studies on the primary bromide obtained from neopentyl alcohol are being continued.

Summary

1. The inactivity of neopentyl alcohol to heat and reagents has been demonstrated.

2. The composition of the bromide mixture obtained from neopentyl alcohol has been further studied and found to consist mainly of rearrangement products.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE HOFMANN REARRANGEMENT OF THE AMIDE OF TERTIARY BUTYLACETIC ACID AND ITS SIGNIFICANCE IN THE THEORY OF REARRANGEMENTS[1,2]

BY FRANK C. WHITMORE AND AUGUST H. HOMEYER

RECEIVED MAY 17, 1932 PUBLISHED AUGUST 5, 1932

In the Hofmann rearrangement of N-halogen amides, the migrating group has been regarded as positive by Jones[3] and as negative by Stieglitz.[4] The stability of the migrating group is shown by the more recent work of Hellerman[5] and of Wallis.[6] Although the stability of the opti-

$$(C_6H_5)_3CCH_2CONH_2 \longrightarrow (C_6H_5)_3CCH_2NH_2$$
$$d\text{-}(C_6H_5CH_2)(CH_3)CHCONH_2 \longrightarrow d\text{-}(C_6H_5CH_2)(CH_3)CHNH_2$$

[1] See THIS JOURNAL, p. 3274.

[2] Submitted by August H. Homeyer (Mallinckrodt Fellow) in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[3] Jones, *Am. Chem. J.*, **50**, 441 (1913); Jones and Hurd, THIS JOURNAL, **43**, 2422 (1921); Jones and Wallis, *ibid.*, **48**, 169 (1926).

[4] Stieglitz and Leech, *ibid.*, **36**, 280 (1914); Stieglitz and Stagner, *ibid.*, **38**, 2047 (1916).

[5] Hellerman, *ibid.*, **49**, 1735 (1927).

[6] Wallis and Nagel, *ibid.*, **53**, 2787 (1931).

cally active migrating group in the latter case has been assumed to be due to a stable positive radical or carbonium ion, it can be explained equally well on the basis of a stable negative radical.[7]

In the present study it has been found that the amide of tertiary butylacetic acid reacts with sodium hypobromite to give a quantitative yield of neopentylamine and none of the tertiary amylamine which would be formed by a rearrangement of the migrating fragment. This marked difference in the behavior of the neopentyl group in different classes of compounds is best pictured on the basis that when the neopentyl group is deprived of an electron pair, it rearranges and when it is not so deprived it does not rearrange. The break in the molecules may be represented as follows

$$(CH_3)_3C:\overset{H}{\underset{H}{C}}\Big| :\ddot{O}:H \longrightarrow \text{Rearrangement within neopentyl group}^{8}$$

$$(CH_3)_3C:\overset{H}{\underset{H}{C}}:\Big| CONH_2 \longrightarrow (CH_3)_3C:\overset{H}{\underset{H}{C}}:NH_2$$

No rearrangement within the neopentyl group

Experimental Part

Rearrangement of Tertiary Butylacetamide to Neopentylamine.—Two and four-tenths cc. of bromine was added dropwise to a stirred solution of 7.2 g. of sodium hydroxide in 60 cc. of water cooled to 0°. To the clear yellow solution was added immediately 3.50 g. of *tert.*-butylacetamide, m. p. 131°, and stirring was continued at 0° for an hour after the amide had dissolved. Then the reaction mixture was allowed to warm slowly. At room temperature a yellow turbidity appeared; at about 50° the solution became colorless and an oily layer separated. After adding 100 cc. of water the reaction mixture was distilled until no more oil came over. The distillate was collected in dilute hydrochloric acid, giving a yellow solution which became colorless on heating and yielded neopentylamine hydrochloride as a white crystalline residue on evaporation. This was taken up in absolute alcohol, evaporated to dryness and washed with ether. After keeping *in vacuo* until constant weight was obtained, the product weighed 3.60 g. (theoretical yield, 3.76 g.) and melted with decomposition *ca.* 273°. Freund and Lenze[9] give the melting point of neopentylamine hydrochloride as *ca.* 275°.

Neopentylamine was identified by preparing the several derivatives described below. The melting points are uncorrected.

Sym.-Neopentylphenylthiourea.—The free amine liberated from 0.63 g. of its hydrochloride by adding excess dilute sodium hydroxide was extracted with ether, dried over anhydrous sodium sulfate and mixed with 0.60 g. of phenyl isothiocyanate. After concentrating, the thiourea was precipitated by adding petroleum ether. The product weighed 0.86 g. (theoretical yield 0.98 g.) and melted, without recrystallization, at 134.5°. Freund and Lenze[10] give the melting point of *sym.*-neopentylphenylthiourea as 136°.

Sym.-Neopentylphenylurea was prepared in an analogous manner. The melting point was 155°. Freund and Lenze give 155°.

[7] Private communication from E. S. Wallis.

[8] See THIS JOURNAL, p. 3431.

[9] Freund and Lenze, *Ber.*, **24**, 2156 (1891).

[10] Freund and Lenze, *ibid.*, **23**, 2868 (1890); **24**, 2158 (1891).

Benzoylneopentylamine was prepared from the amine hydrochloride by the Schotten–Baumann method. After recrystallization from petroleum ether it melted at 112–113°.

Rearrangement of Ethyldimethylacetamide.—It was desired to prepare *tert.*-amylamine and its derivatives for purposes of comparison with the neopentylamine. The Hofmann rearrangement of 3.50 g. of ethyldimethylacetamide, m. p. 103°, was carried out as described above. The distillate yielded 2.75 g. of *tert.*-amylamine hydrochloride, m. p. *ca.* 225°. Extraction of the residue in the distilling flask with ether and recrystallization of the product from alcohol gave 0.85 g. of *sym.*-(di-*tert.*-amyl)-urea which sublimed at about 220°.

The urea was identified by fusing with phthalic anhydride[11] to give *tert.*-amylphthalimide. After two recrystallizations from dilute alcohol it melted at 190°. *Tert.*-amylphthalimide was also prepared from the free amine. The melting point was 187–188° and a mixed melting point showed no depression.

Benzoyl-*tert.*-amylamine was prepared from the amine hydrochloride by the Schotten–Baumann method. After recrystallization from petroleum ether it melted at 92–93°. A mixture of this compound (2.2 mg.) with benzoylneopentylamine (2.7 mg.) melted at 77–100°.

Sym.-tert.-amylphenylthiourea prepared by the method described above melted at 117–118°. A mixture of this thiourea (2.5 mg.) with *sym.*-neopentylphenylthiourea (2.1 mg.) melted at 95–99°.

Sym.-tert.-amylphenylurea melted at 130–131°. A mixture of this urea (1.8 mg.) with *sym.*-neopentylphenylurea (2.1 mg.) melted at 100–112°.

Summary

1. *Tert.*-butylacetamide yields neopentylamine quantitatively by the Hofmann rearrangement.

2. The failure of the migrating neopentyl group to rearrange to a *tert.*-amyl group is discussed in its bearing on the mechanism of rearrangements.

3. Apparently a "negative" neopentyl group is stable whereas a "positive" neopentyl group undergoes rearrangement to a *tert.*-amyl group and related compounds.

STATE COLLEGE, PENNSYLVANIA

[11] Tingle and Brenton, THIS JOURNAL, **32**, 113 (1910).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ACTION OF NITROUS ACID WITH TRIMETHYLACETAMIDE[1]

BY FRANK C. WHITMORE AND D. P. LANGLOIS

RECEIVED MAY 17, 1932 PUBLISHED AUGUST 5, 1932

The established fact[2] of the rearrangement of neopentyl alcohol and of neopentylamine when the hydroxyl and amino groups are removed in chemical reactions, caused us to study the corresponding reactions with trimethylacetic acid and its derivatives. The relation of the two sets of compounds is as follows:

$$(CH_3)_3CCH_2X \text{ and } (CH_3)_3C\overset{\overset{O}{\|}}{C}X$$

in which X may be OH, NH_2 or halogen. The entire trimethylacetyl series has been prepared.[3] The literature gives no indication of rearrangement during any of these preparations but also gives no yields.

Nitrous acid reacts with acid amides to give a quantitative yield of nitrogen.[4] No reference to the amount of organic acid formed has been found in the literature.

In the present work, acetamide is shown to give a quantitative yield of acetic acid.

If the action of trimethylacetamide with nitrous acid gave a similar rearrangement to that of neopentylamine, the products might be $(CH_3)_2C(OH)COCH_3$,[5] $CH_2{=}C(CH_3)COCH_3$.[6] No such products were found. Trimethylacetamide (2 moles) was treated with nitrous acid at 30–35°. The products included 1.61 moles of nitrogen, 1.62 moles of trimethylacetic acid and 0.2 mole of unreacted amide. No other products were found.

The absence of rearrangement in reactions involving the trimethylacetyl group is further indicated by the fact that the changes, acid ⟶ acid chloride ⟶ acid amide ⟶ original acid, gave an over-all yield of 79% or an average of 93% for each step. Moreover, these reactions all take place with the greatest ease and at relatively low temperatures. The obvious explanation of these facts is that the initial step in each reaction is an addition to the carbonyl group of the trimethylacetyl, giving intermediate products such as

[1] Presented by D. P. Langlois in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

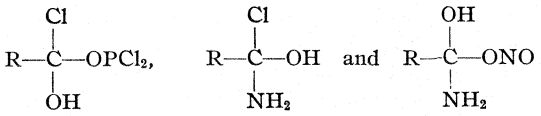
[2] See pp. 3431, 3441.

[3] Butlerow, *Ann.*, **173**, 373 (1874); Meyer, *Monatsh.*, **27**, 36 (1906); Franchimont and Klobbie, *Rec. trav. chim.*, **6**, 238 (1887); Scheuble and Loeble, *Monatsh.*, **25**, 1095 (1904); Aschan, *Ber.*, **31**, 2344 (1898).

[4] Plimmer, *J. Chem. Soc.*, **127**, 2651 (1925).

[5] Scheibler and Fisher, *Ber.*, **55**, 2915 (1922).

[6] Beilstein, "Handbuch," 4th ed., Vol. I, p. 733.



which then become RCOCl, $RCONH_2$ and RCOOH, respectively. No one of these changes gives an intermediate ion which might cause a rearrangement.

On the other hand, reactions of neopentyl compounds must take place either through an initial ionization (Meerwein) or, more probably, through compound formation (oxonium or ammonium) with the hydroxyl or amino group attached to the neopentyl system. At the instant this oxonium or ammonium compound changes to give a stable inorganic molecule such as water or nitrogen, the neopentyl group is left with only 30 valence electrons and is consequently unstable.[7]

Experimental

Preparation of Trimethylacetamide.—Trimethylacetic acid was made according to "Organic Syntheses" (Vol. VIII, 1928, p. 104). Two moles (204 g.) of the acid was warmed on a steam-bath under a reflux condenser with 138 g. (50% excess) of phosphorus trichloride. Very little hydrogen chloride escaped. Two layers separated. After heating for one and a half hours, the mixture was cooled in ice. The acid chloride was decanted from the sirupy bottom layer and added to 1 liter of concentrated aqueous ammonia cooled to 0°. The white amide was filtered off and dried *in vacuo* over sulfuric acid. It was heated with 600 cc. of ethyl acetate and filtered hot to remove ammonium chloride. The solution was evaporated until crystals began to appear and 1200 cc. of petroleum ether was added. The mixture was heated to give a clear solution and then allowed to cool slowly. It was finally cooled in a refrigerator and filtered. The trimethylacetamide melted at 155–157°; yield 176.5 g. or 87% of the calculated amount based on the trimethylacetic acid used. Further crystallization did not change the melting point.

Action of Nitrous Acid on Acetamide.—One-half mole (29.5 g.) of acetamide (dried over phosphorus pentoxide) and 34.5 g. (0.5 mole) of sodium nitrite were dissolved in 350 cc. of water. The mixture was placed in an open flask fitted with a stirrer and a dropping funnel. To the mixture was added slowly with constant stirring 15 cc. of concentrated sulfuric acid in 100 cc. of water. After the addition of the acid another 34.5 g. of sodium nitrite was added and another 15 cc. of sulfuric acid in 100 cc. of water was added slowly. The mixture was stirred for six hours after all of the acid had been added. The temperature was kept at 50–60° during the addition of the acid and at 30–35° during the final stirring. The mixture was then heated for half an hour at 80° to drive off the excess nitrogen oxides and then distilled until no more acetic acid came over. The distillate was diluted to 1 liter in a volumetric flask and the acetic acid titrated, using 10-cc. portions; 10 cc. of the acid required 19 cc. of 0.2700 *N* base. Hence the acid was 0.513 *N*, and 0.51 mole of acid was obtained from 0.50 mole of acetamide.

Action of Nitrous Acid on Trimethylacetamide.—One mole of sulfuric acid was diluted to 2 liters and 2 moles of trimethylacetamide (202 g.) was dissolved in it. The mixture was warmed to 60° to effect solution. It was placed in a three-necked 5-liter flask and cooled. The flask was fitted with a mercury-sealed stirrer, a dropping funnel and an exit tube for gases. This tube was connected with an absorption train, consisting

[7] See p. 3279.

of two ordinary wide-mouthed bottles fitted with bubblers and a Friedrich absorption tower, and a gas meter for measuring the gas evolved. The absorption train was filled with a saturated solution of potassium permanganate about 0.5 *N* in sulfuric acid. This was to remove any nitrogen oxides formed during the reaction, thus leaving pure nitrogen to be measured.

When the solution in the flask had cooled to 35°, stirring was started and a solution of 2 moles (138 g.) of sodium nitrite in 1 liter of water was run in at the rate of 1 cc. per minute. After this addition another half mole of sulfuric acid was run in and another mole of sodium nitrite (69 g.) in 500 cc. of water was added as before. The entire addition required about forty-eight hours. Stirring was continued another forty-eight hours as long as gas was evolved. An oily layer of trimethylacetic acid separated. The nitrogen evolved occupied 44 liters at an average temperature of 30° and an average pressure of 743 mm., thus amounting to 1.61 moles.

The contents of the reaction flask were poured out and the two layers separated. The water layer was extracted with four 250-cc. portions of ether, and the ether extracts combined with the acid layer. The water layer was reserved (1). The ether solution was extracted with three 150-cc. portions of 20% sodium hydroxide and the ether residue was reserved (2). The sodium hydroxide extract was heated to distil off the ether and any other volatile organic product. The distillate was reserved (3).

The sodium hydroxide solution was then cooled and acidified with sulfuric acid. A layer of trimethylacetic acid separated and was drawn off. The water layer was distilled until no more oily drops came over. The distillate was saturated with salt and the layer of acid drawn off. This water residue was then distilled until no more oily drops came over and the distillate was saturated with salt. The layer of acid was drawn off and all three lots of acid were combined. Twenty cc. of ether was added to the acid and the mixture was dried over sodium sulfate in the refrigerator. The solution was then distilled.

Fraction	B. p., °C.	Press., mm.	Weight
1	35– 55	743	15 cc.
2	55–162	743	1.5 g.
3	162–163	743	165 g.
4	Very little solid residue		

The 165 g. of the acid obtained is 1.62 moles.

The water layer (1) was made strongly alkaline with sodium hydroxide and cooled. It was extracted with six 200-cc. portions of ethyl acetate. The ethyl acetate was evaporated on a water-bath and 12 g. of a dry solid was obtained, m. p. 155–156° (unreacted trimethylacetamide). No other product could be detected.

The ether residue (2) was distilled on a water-bath. All of the volatile material came over at 35–55°, leaving 8 g. of a dry white solid, m. p. 155–157° (unreacted trimethylacetamide). No other product could be detected.

The distillate (3) was again distilled. Ether came over at 35°. There was then a gradual rise in temperature, more rapid toward the last, until it reached 98°, where it remained constant until all had distilled. Apparently it contained nothing but ether and water.

Summary

1. Trimethylacetamide reacts with nitrous acid to give over 90% of the calculated amounts of nitrogen and trimethylacetic acid.

2. The reactions of derivatives of trimethylacetyl give no rearrange-

ments. This is in marked contrast to the rearrangements of the analogous neopentyl derivatives.

3. The significance of this absence of rearrangement in relation to the mechanism of rearrangements is discussed.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

REARRANGEMENTS INVOLVED IN THE ACTION OF NITROUS ACID WITH NORMAL-BUTYLAMINE[1]

BY FRANK C. WHITMORE AND D. P. LANGLOIS

RECEIVED MAY 17, 1932 PUBLISHED AUGUST 5, 1932

The recorded data[2] on the reaction of nitrous acid and primary aliphatic amines make it of the utmost importance in the theory of rearrangements.[3] For instance, it can hardly be argued that a primary amine undergoes an "ionization" into R^+ and NH_2^- similar to that which is sometimes assumed as part of the mechanism of the rearrangement of carbinols (Meerwein). Moreover, this reaction results in the formation of olefins under conditions which would not cause the dehydration of even a tertiary alcohol.

n-Propylamine reacts with nitrous acid to give *n*-propyl alcohol, isopropyl alcohol and propylene.[4] Isobutylamine gives tertiary butyl alcohol[5] and isobutylene. No other organic products are mentioned. *n*-Butylamine is reported to give *n*-butyl alcohol and isobutyl alcohol.[6] Other workers report *n*-butyl alcohol, secondary butyl alcohol, *n*-butenes and dibutyl nitrosamine but *no* isobutyl alcohol.[7]

Neopentylamine gives only the rearrangement product, tertiary amyl alcohol.[8]

n-Butylamine was chosen for the present study because of the simplicity of its molecule and the disagreement in the literature regarding its behavior with nitrous acid. The amine was prepared from very pure *n*-butyl bromide obtained from highly purified *n*-butyl alcohol. The yields of products of the action of nitrous acid were as follows

[1] Presented by D. P. Langlois in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Porter, "Molecular Rearrangements," p. 140 (1928).

[3] See p. 3281.

[4] Siersch, *Ann.*, **144,** 140 (1867); Linnemann, *ibid.*, **161,** 44 (1872); *Ber.*, **10,** 1111 (1877); Meyer and Forster, *ibid.*, **9,** 535 (1876).

[5] Linnemann, *Ann.*, **162,** 24 (1872).

[6] Linnemann and Zotta, *ibid.*, **162,** 5 (1872); Ray and Rakshit, *J. Chem. Soc.*, **101,** 141 (1912).

[7] Meyer, Barbieri and Forster, *Ber.*, **10,** 132 (1877).

[8] Freund and Lenze, *Ber.*, **24,** 2150 (1891).

n-Butyl alcohol	25.0%
Sec.-butyl alcohol	13.2
n-Butyl chloride	5.2
Sec.-butyl chloride	2.8
n-Butenes	36.5
High boiling material	7.6
Butyl nitrites, traces	..
Total	90.3%

No trace of isobutyl alcohol, tertiary butyl alcohol or isobutylene was detected. The formation of the *n*- and *sec.*-butyl chlorides was unexpected. Their formation represents a new reaction in aliphatic chemistry and gives added evidence for the momentary existence of R^+ as an intermediate in the reaction, since it is most improbable that the alcohols were first formed and then were converted to chlorides in the barely acid solution. To get additional evidence on this new reaction, *n*-butylamine in calcium chloride solution was treated with calcium nitrite and hydrochloric acid. The increased concentration of chloride ion raised the yields of *n*- and *sec.*-butyl chlorides to 9.5 and 6.3%, respectively. The fact that the *n*-butyl chloride predominates indicates that the *n*-butenes are not intermediates in the process. Moreover, it is hardly conceivable that *n*-butenes could add hydrogen chloride under the conditions of the experiment. Further, the *n*-butenes could not have been formed by dehydration of the *n*- and *sec.*-butyl alcohols under the conditions of the experiment. The alcohols, halides and olefins are products of simultaneous reactions and are not formed from each other. Thus all evidence points to the validity of the suggested mechanism for the reaction of *n*-butylamine with nitrous acid.

$$CH_3CH_2:\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}}:\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}}:\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{N}}}:H + HNO_2 \longrightarrow CH_3CH_2:\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}}:\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}} + N_2 + H_2O + OH^-$$

The formation, from the amine nitrite, of a molecule of nitrogen, one of water, and an hydroxyl ion, each with its necessary number of electrons, leaves the end carbon of the *n*-butyl group with only six electrons. Such a product is capable of only momentary existence.[9] It unites with ions from the solution giving the observed products, *n*-butyl alcohol, chloride and nitrite. It also changes monomolecularly by (a) losing a proton to give butene-1, and (b) undergoing a shift of an electron pair and its proton to form a positive *sec.*-butyl group. This unites with ions from the solution forming *sec.*-butyl alcohol, chloride and nitrite. It also loses protons to give butene-1 and butene-2. The *sec.*-butyl ion could undergo a shift of an electron pair with a methyl to give an isobutyl ion, which could unite with ions to give isobutyl alcohol, etc., or could give isobutylene. Since no forked four-carbon products were formed, it is evident that the shift of a

[9] See p. 3277.

methyl does not take place under the conditions of these experiments. It is interesting, however, that Linnemann and Zotta, and Ray and Rakshit found such forked compounds when working at higher temperatures.

Experimental

Distillation of *n*-Butyl Alcohol.—Forty-five liters of the best commercial grade of *n*-butyl alcohol[10] was distilled through an adiabatic packed column, 8.3 meters high and 7.6 cm. in diameter.[11] At the start a reflux ratio of about 80:1 was used. After 1300 cc. of the alcohol had distilled, the refractive index became constant (n_D^{20} 1.3990). The reflux ratio was then dropped to 50:1 for the next 10 liters of distillate. The refractive index rose only 0.0001. Then 25 liters was distilled with the ratio 10:1 without any change in the refractive index. The residue of 7.5 liters was slightly brown. In all, fifty fractions were collected. The middle fractions were used in the present studies. They boiled at 116.2–116.4° (744 mm.) (Cottrell) and showed n_D^{20} 1.3991.

Preparation and Purification of *n*-Butyl Bromide.—The methods of "Organic Syntheses" [Vol. I, 1921, p. 5] were used. A 48-mole run of the purified *n*-butyl alcohol gave an 86% yield of crude *n*-butyl bromide all boiling at 95–100° (735 mm.). The crude bromide was distilled through a 150 × 2 cm. column[12] using a reflux ratio of 30:1. Three low fractions were obtained, 190 g. at 95–99°, 178 g. at 99–99.5° and 425 g. at 99.5–100°. The first two contained water. The main fraction consisted of 4.2 kg. boiling at 100° (741 mm.), n_D^{20} 1.4395. The residue was 190 g.

Preparation and Purification of *n*-Butylamine.—Two 12-liter flasks were fitted with stirrers and 8 liters of 90% alcohol placed in each. Ammonia was run in with constant stirring until the flasks had gained about 300 g. in weight. Into each flask was run 0.5 mole (68.5 g.) of *n*-butyl bromide. A slow stream of ammonia was allowed to pass through the flasks during the reaction to ensure complete saturation so that the ratio of ammonia to bromide was kept high. Altogether 11 moles of the bromide was added at the rate of 0.5 mole to each flask every four hours. This varied slightly during the night. At the end of the addition the mixture was stirred for two days longer until no bromide could be detected. It was then distilled to remove the alcohol. After about 8 liters of alcohol had been removed from the combined flasks, ammonium bromide separated and was filtered off. Eight more liters of alcohol solution was distilled off and more ammonium bromide filtered off. A total of 378 g. was obtained. About 2 liters of solution remained in the flask. To this was added 2 liters of water. The mixture was distilled to remove the last traces of alcohol. This was repeated until no alcohol remained.

Without cooling the solution there was added 12 moles of sodium hydroxide in 2 liters of water and the mixture was distilled until the lower boiling substance had come over. It was then allowed to cool. The distillate was dried over fused potassium hydroxide.

The two layers in the reaction flask were separated and the oily amine layer was dried over fused potassium hydroxide. More sodium hydroxide was added to the water layer but no more amine separated. Since extraction of a small portion of the water layer with ether showed only very small amounts of the amine, it did not seem advisable to extract the whole water layer of over 4 liters.

---

[10] Through the courtesy of C. L. Gabriel of the Commercial Solvents Corporation a middle cut was obtained from a batch distillation of 30,000 gallons of *n*-butanol.

[11] The construction and operation of this column have been described in detail by Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[12] See p. 3451.

The amine was fractionated through the 150-cm. glass-packed column.[13] Nothing came over below 76.5°, then 383.5 g. distilled at 76.5°(742 mm.). At this point the amine ceased to distil. By heating the column and increasing the heat on the flask more amine was forced up the column but the temperature began to climb rapidly, indicating the presence of dibutylamine. The yield of pure *n*-butylamine was 47%; n_D^{20} 1.4008.

Reaction of *n*-Butylamine with Nitrous Acid.—The following is a typical run. *n*-Butylamine (1 mole) was dissolved in 1 liter of water and neutralized with the calculated quantity of 6 *N* hydrochloric acid. This was placed in a round-bottomed flask fitted with a mercury-sealed stirrer, a dropping funnel and an outlet tube for gas. A solution of three moles of sodium nitrite in a minimum quantity of water was added to the cold amine hydrochloride solution. No reaction occurred in the cold.

The outlet tube was connected with the following train: a spiral condenser with a receiver cooled in an ice-bath to remove the condensable materials; two calcium chloride and one phosphorus pentoxide drying towers; a series of three 250-cc. absorption bottles containing absolute alcohol for the absorption of butenes; an absorption tower containing alkaline permanganate solution (50 g. of potassium permanganate and 20 g. of potassium hydroxide per liter) for the absorption of nitrogen oxides; and finally a large graduated carboy for collecting and measuring the nitrogen evolved. The dropping funnel of the apparatus was filled with 1 *N* hydrochloric acid.

After sealing the apparatus, the stirrer was started and the flask slowly heated until the solution boiled. A rather rapid evolution of gas occurred and considerable volatile material collected in the receiver. Heating was continued until the volume of nitrogen increased only slowly. The reaction was then stopped. A very slow stream of 1 *N* hydrochloric acid was added during the reaction to prevent the solution from becoming alkaline due to the hydrolysis of the sodium nitrite. Samples of gas were removed during the reaction from various positions along the train to test the completeness of absorption of the butenes and nitrogen oxides.

The condensed material which consisted of an oily layer and a water layer was saturated with sodium chloride and a few cc. of 1 *N* hydrochloric acid was added to remove any amine which had distilled over. The two layers were separated and the water layer extracted with ether. The ether was removed and the residue added to the oily layer, which was dried over anhydrous potassium carbonate. The amine was recovered by making the water layer alkaline with sodium hydroxide and extracting with ether. The dried oily layer was fractionated through a partial condensation column 90 × 1.2 cm.[14]

The butenes were recovered by running the alcoholic solution into warm water and collecting the evolved gas.

Reaction 1.—A total of 3.5 moles (255.5 g.) of *n*-butylamine was treated with 10.5 moles (724.5 g.) of sodium nitrite by the procedure indicated. A fractionation of the condensed material gave the following fractions.

Fraction	B. p., °C.	Pressure, mm.	n_D^{20}	Wt., g.
1	66–68	744	1.3981	7
2	68–76	744		0.5
3	76–80	744	1.4085	13
4	80–97.6	744		1.1
5	97.6–98.4	742	1.3970	26.3
6	98.4–114.6	742		1.3
7	114.6–116.2	742	1.3991	50.0
8	Higher boiling material			15.0

[13] See p. 3451.

[14] See p. 3453.

Fraction 1 was chiefly *sec.*-butyl chloride. It was identified by the method of Johnson,[15] yielding an anilide, m. p. 106–108°; mixed melting point with a pure sample of methylethylacetanilide prepared from *sec.*-butyl bromide, 106–108°. Some *sec.*-butyl nitrite was present (odor) but it was impossible to separate it by distillation since the two boiling points are so close together. A small amount of the material was refluxed for an hour with potassium carbonate solution and the aqueous solution gave a distinct test for nitrite ion.

Fraction 3 was chiefly *n*-butyl chloride. It was also identified by the method of Johnson,[15] yielding an anilide, m. p. 58–59°; mixed melting point with a pure sample of *n*-valeranilide 58–61°. The chlorine analysis of the fraction indicated the presence of some substance besides *n*-butyl chloride. Found: 33.1% Cl; calcd. for C_4H_9Cl, 38.8%. The index of refraction was high for *n*-butyl chloride. *n*-Butyl nitrite was present. Boiling some of the material with potassium carbonate solution gave nitrite ion. The odor of an organic nitrite was always obtained from material in Fractions 1 and 3.

Fraction 5 had the boiling point and index of refraction of *sec.*-butyl alcohol.

Fraction 7 was *n*-butyl alcohol. It had the correct boiling point and index of refraction. With 3,5-dinitrobenzoyl chloride it gave an ester melting at 62–64°, mixed melting point with a sample of pure *n*-butyl 3,5-dinitrobenzoate 62–64°.

Fraction 8 was unidentified but may have been the same as the dibutylnitrosamine obtained by v. Meyer.[16]

Butenes.—25.2 liters of butenes at 24° and 727 mm. was obtained from Reaction 1. Calculated to standard conditions, this gives 22.1 liters or 55.2 g.

In order to test for the presence of isobutene in the gas the method of analysis of Marcowitch and Moore[17] was used. This method depends on the relative rate of absorption of isobutene and the *n*-butenes in 68% sulfuric acid. No attempt was made to distinguish between the *n*-butenes.

The apparatus consisted of an Orsat absorption pipet and a gas-measuring buret. The rate of absorption was determined by measuring the decrease in volume of the gas standing in contact with the acid for five-minute periods.[18]

Samples of isobutene and the *n*-butenes were prepared according to the method of Davis[19] and the rate of absorption of a 50% mixture of each gas with air was determined. The result is plotted on Fig. 1. The isobutene is quantitatively absorbed in twenty minutes while only 15% of the *n*-butenes is absorbed in the same time. Synthetic mixtures of isobutene with the *n*-butenes were then prepared and the rate of absorption determined as before. These results are also plotted on Fig. 1. The curves for the mixtures show a rapid absorption for the first five or ten minutes and then a sharp decrease in the rate until a final slow constant rate is obtained. From a consideration of the curves for the pure butenes it is evident that the final slow rate of absorption is due to the *n*-butenes and that they have been absorbed at this constant rate from the beginning. We can then calculate the percentage of isobutene in the mixture by taking the total absorption and subtracting from it the quantity of *n*-butenes absorbed. This latter factor is obtained by taking the amount of gas absorbed in five minutes as indicated by the final slope of the line and multiplying by the number of five-minute intervals. This may be read directly from the graph by extending the straight line portion of the curve until it intersects the ordinate axis, taking the percentage of isobutene to be that corresponding to the intersection on the axis. In this manner results with a precision of

[15] Johnson, THIS JOURNAL, **53**, 1063 (1931).

[16] V. Meyer, *Ber.*, **10**, 132 (1877).

[17] Marcowitch and Moore, *Natl. Pet. News*, Oct. 14 and 21, 1931.

[18] Fresh acid was introduced after every third run.

[19] See THIS JOURNAL, **50**, 2778 (1928).

about 1% can be obtained. The following results were calculated for the curves in Fig. 1.

Curve	Gas mixture *n*-Butenes, cc.	Gas mixture Isobutene, cc.	Isobutene taken, %	Isobutene calcd., %
2	78.1	3.7	4.9	5.2
3	48.0	4.0	7.7	7.6
4	86.0	12.6	12.8	13.2
5	51.7	22.7	30.5	29.8
6	60.1	29.1	32.6	30.7

Figure 2 represents the absorption curve of the butenes obtained from Reaction 1. It is practically identical with the curve for *n*-butenes given in Fig. 1. There is a slightly

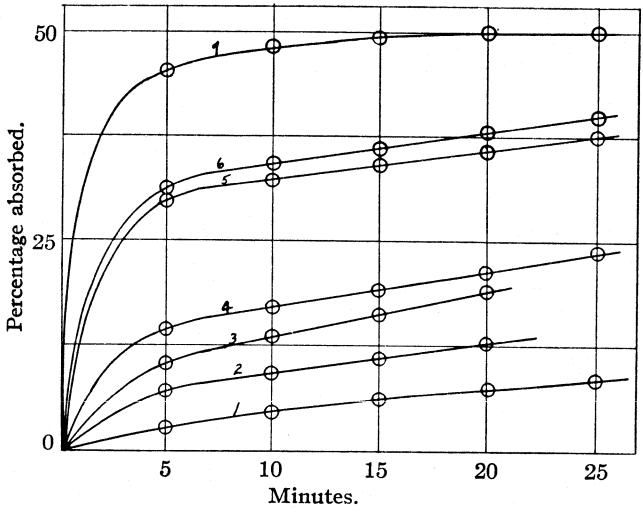


Fig. 1.—1, 50% *n*-butenes, 50% air; 2, 4.9% isobutene; 3, 7.7% isobutene; 4, 12.8% isobutene; 5, 30.5% isobutene; 6, 32.6% isobutene; 7, 50% isobutene, 50% air. 2–6, isobutene + *n*-butenes = 100%.

greater absorption during the first five minutes than during the subsequent five-minute intervals which amounts to about 0.5%. This behavior is also shown by the curve for

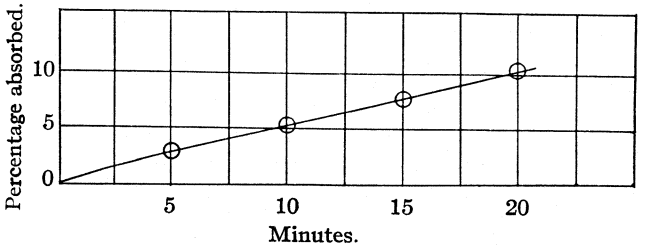


Fig. 2.—79% butenes, 21% air.

the *n*-butenes, so that it is evident that isobutene is not present in amounts greater than 1% in the gas from Reaction 1.

The dibromide was prepared by passing the butene into bromine in carbon tetrachloride. The product was fractionated through a 62 × 2.3 cm. packed total reflux column.[20] Only one fraction was obtained boiling at 153–158° at 728 mm. Apparently no isobutylene dibromide (b. p. 148°) was present.

No tertiary butyl alcohol, isobutyl alcohol or isobutylene could be detected.

Reaction 2.—This reaction was carried out in the presence of a higher concentration of chloride ion. One mole of *n*-butylamine in a solution of 1.5 moles of calcium chloride was treated with 1 mole of calcium nitrite. (The latter was used instead of sodium nitrite to prevent the precipitation of part of the chloride ion as sodium chloride.) The usual procedure was used and the products of reaction were separated and identified as in Reaction 1.

	Weight, g.	Yield based on amine consumed, %
n-Butyl chloride	4.4	9.5
Sec.-butyl chloride	2.9	6.3
Mixture of *n*- and *sec.*-butyl alcohols	14.7	39.6
n-Butenes	10.5	37.6
		93.0

Unreacted amine recovered, 36.1 g. (0.5 mole). No isobutyl alcohol, *tert.*-butyl alcohol or isobutylene was detected.

Reaction 3.—This reaction was carried out in the presence of freshly precipitated copper. Half a mole of *n*-butylamine (36.5 g.) in the presence of 60 g. of moist freshly precipitated copper was treated with 1.5 moles of sodium nitrite by the usual procedure. The copper reacted readily to give cuprous chloride but most of the amine was recovered unchanged.

Oily material	5.4 g.	
n-Butenes	5.32 g.	(43.6% yield based on amine consumed)
Unreacted amine recovered	21 g.	(0.29 mole)

Summary

1. *n*-Butylamine reacts with nitrous acid to give the alcohols and chlorides and traces of nitrites of *n*- and *sec.*-butyl together with butene-1 and -2. No branched chain butyl compounds have been detected.

2. The relation of these facts to the mechanism of rearrangements is discussed.

STATE COLLEGE, PENNSYLVANIA

[20] See p. 3451.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ABSENCE OF REARRANGEMENT OF THE ISOBUTYL GROUP DURING THE FORMATION OF ISOBUTYLMAGNESIUM BROMIDE AND ITS RELATION TO THE THEORY OF REARRANGEMENTS[1]

BY FRANK C. WHITMORE AND ALBERT R. LUX

RECEIVED MAY 17, 1932 PUBLISHED AUGUST 5, 1932

The ready change of isobutyl compounds to tertiary butyl compounds has long been known. The interconversion of the bromides has been thoroughly studied.[2] The results of these studies indicate that (1) rearrangement of isobutyl bromide to tertiary butyl bromide at high temperatures in the *vapor phase* may occur by way of dissociation and addition of hydrogen bromide (Brunel) but (2) this rearrangement takes place more readily in the liquid phase and at temperatures at which there is no dissociation into hydrogen bromide and olefin. Heating the *vapor* of isobutyl bromide at 140° for fourteen hours produces no rearrangement while heating the *liquid* at the same temperature for *one* hour gives a 55% conversion to the tertiary bromide (Michael). The isobutyl "ions" readily rearrange by the transfer of an electron pair and its proton.[3]

Other isobutyl compounds undergo similar rearrangements. Isobutyl iodide reacts with silver acetate in the absence of a solvent to give isobutyl acetate while the presence of acetic acid as a solvent makes tertiary butyl acetate the chief product.[4] Similar results are obtained with silver cyanate.[5] With silver oxide in the presence of acetic acid, isobutyl bromide yields tertiary butyl alcohol and tertiary butyl acetate (Linnemann). An even more interesting example of this transformation is the conversion of isobutyl iodide to tertiary butyl chloride by the action of iodine monochloride (Linnemann). This reaction apparently occurs as follows

$$(CH_3)_2CHCH_2\boxed{:\ddot{I}: + :\ddot{I}}:\ddot{Cl}: \longrightarrow I_2 + \bar{Cl} + (CH_3)_2CHCH_2^+$$

The two ions left are peculiar in that each is the result of a "chemical reaction" rather than of an ordinary "ionization." Each is present only in

[1] Presented by Albert R. Lux in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. See p. 3274.

[2] Elketoff, *Ber.*, **6**, 1258 (1873); Meyer and Pond, *ibid.*, **18**, 1623 (1885); Faworsky, *Ann.*, **354**, 327 (1907); Michael and Leupold, *ibid.*, **379**, 263 (1911); Brunel, *Ber.*, **44**, 1000 (1911); *Ann.*, **384**, 245 (1911); THIS JOURNAL, **39**, 1978 (1917); Michael and Zeidler, *Ann.*, **393**, 81 (1912); Michael Scharf and Voight, THIS JOURNAL, **38**, 653 (1916); Meerwein and van Emster, *Ber.*, **55**, 2520 (1922); W. Hückel, "Theoretische Grundlagen der organischen Chemie," Leipzig, 1931, Vol. I, pp. 205–207.

[3] See p. 3278.

[4] Linnemann, *Ann.*, **162**, 12 (1872).

[5] Brauner, *Ber.*, **12**, 1874 (1879).

small concentrations. This apparently favors the monomolecular rearrangement.

$$(CH_3)_2CHCH_2^{\oplus} \longrightarrow (CH_3)_3C^{\oplus}$$

The literature contains no definite indication regarding a rearrangement of the isobutyl group during the formation or reaction of the Grignard reagent.[6] This reaction was interesting to us because of the following relations:

$$ROH + \text{an electrically neutral compound} \longrightarrow H_2O + R^+ \qquad (1)$$

If the hydroxyl is removed with the octet of the oxygen complete, the carbon to which it was attached must at some instant have only six electrons.[7] Similarly

$$RX + \text{an electrically neutral compound} \longrightarrow MX + R^+ \qquad (2)$$

In each case the R^+ may undergo rearrangement before combining with a negative ion from the reaction mixture. (3) On the other hand, if RX is treated with an electrically neutral *element* such as magnesium or sodium, the possible intermediate products are more varied. Thus

$$R:\ddot{\underset{\cdot\cdot}{X}}: + \underset{\text{(atom)}}{Mg:} \longrightarrow \left[:\ddot{\underset{\cdot\cdot}{X}}:Mg\right]^+ + R: \qquad (1)$$

$$\longrightarrow \left[:\ddot{\underset{\cdot\cdot}{X}}:Mg\cdot\right]^{\circ} + R\cdot \qquad (2)$$

$$\longrightarrow \left[:\ddot{\underset{\cdot\cdot}{X}}:Mg:\right]^- + R^+ \qquad (3)$$

In each case the pictured intermediate products can combine to form RMgX. A consideration of the three possible processes in detail is instructive. The first could give no rearrangement, since the organic radical has its full complement of electrons. Since there is no source of protons present, it can only combine with the MgX^+. The free R· radicals formed according to (2) might combine to give R:R or might disproportionate.

$$2R\cdot \longrightarrow R: + R^+$$

The R^+ could merely lose a proton to the R: or it could first rearrange and then lose a proton. In all cases studied to date, these two possible processes give the same product. Cases in which different products could be formed are being studied in this Laboratory in connection with both the Grignard and Wurtz reactions. If the third picture is correct, the R^+ should rearrange at least in part and the rearranged product could then give the corresponding Grignard reagent.

[6] Gilman and Heck, *Bull. soc. chim.*, [4] **45**, 1095 (1929). Other rearrangements involving the Grignard reagent are recorded in the literature as follows: Richard, *Ann., chim. phys.*, [8] **21**, 342 (1908); Tiffeneau and Delange, *Compt. rend.*, **139**, 573 (1903); Gilman and Kirby, THIS JOURNAL, **51**, 3475 (1929); **54**, 345 (1932); Gilman and Harris, *ibid.*, **53**, 3541 (1931); Austin and Johnson, *ibid.*, **54**, 647 (1932).

[7] This is on the simple assumption that the subtraction of eight electrons from the fourteen electrons originally associated with the carbon and its attached oxygen leaves only six with the carbon.

In the present study isobutyl bromide (5 moles) containing less than 0.5% of tertiary bromide was converted to 3.7 moles of Grignard reagent and 0.8 mole of gas consisting mainly of isobutylene and isobutane.[8] The Grignard solution was diluted with dry ether and treated with oxygen at 0°. The resulting ROMgBr product was decomposed by ammonium sulfate solution and the resulting alcohol was fractionally distilled through special columns and tested for tertiary butyl alcohol by procedures found effective with mixtures containing 2% of tertiary butyl alcohol in isobutyl alcohol. No tertiary butyl alcohol was detected. When the Grignard solution from tertiary butyl chloride was similarly treated, an 80% yield of the alcohol was obtained.

These experiments practically eliminate process (3) from consideration. This study is being continued.

Experimental

Preparation of Isobutyl Bromide.—In a 3-liter three-necked flask provided with an efficient stirrer, a thermometer and a dropping funnel, was placed 1036 g. (14 moles) of isobutyl alcohol, b. p. 107–108°. After cooling to −4°, 1390 g. (5.1 moles) of phosphorus tribromide was added during six hours, with vigorous stirring and below −1° at all times. The cooling bath was removed and the mixture was allowed to stand for twelve hours. The mixture was then distilled through a short column using the vacuum of a water pump. The bromide was not heated above 50°. Much hydrogen bromide was evolved during the distillation. The crude bromide was shaken with 50 g. of anhydrous potassium carbonate and allowed to stand for two days with 25 g. of freshly calcined potassium carbonate. The latter was removed and the bromide was distilled under reduced pressure through an 85 × 2 cm. packed column of the total condensation, adjustable take-off type (Fig. 1). The isobutyl bromide was collected at 41.5–42.2° (137 mm.), yield 1060 g. (55% of the theoretical amount).

Analysis of Isobutyl Bromide for Tertiary Butyl Bromide.—The method of Michael and Leupold[2] was used. It depends on the fact that cold distilled water will hydrolyze *tert.*-butyl bromide but will not react with the isobutyl compound. The hydrogen bromide formed is conveniently determined by the Volhard method.

The isobutyl bromide prepared above was found to contain about 0.6% of tertiary bromide.

Further Purification of Isobutyl Bromide.—About 1 kg. of this isobutyl bromide was stirred with 300 cc. of distilled water for five hours. After washing with a fresh portion of distilled water, the bromide layer was dried over potassium carbonate and fractionated through the 85 × 2 cm. column. Over 80% of the bromide was recovered at 41.8–42.5° (135 mm.); d_4^{20} 1.266, n_D^{20} 1.4363.

Anal. Calcd. for C_4H_9Br: Br, 58.3. Found: Br, 58.5, 58.2; tertiary bromide, 0.37, 0.29%.

Preparation of Isobutylmagnesium Bromide.—A 2-liter three-necked flask was fitted with a mercury-sealed stirrer; a thermometer, an efficient reflux condenser and a 500-cc. dropping funnel. The condenser was connected to two traps, the first cooled with ice and the second with solid carbon dioxide and acetone.

To 120 g. of magnesium turnings and a crystal of iodine was added a small amount

[8] The exact composition of this gas and the effect of varying conditions on its composition are being studied in relation to the theory of the Grignard reaction.

of the purified isobutyl bromide in dry ether. As soon as the reaction started, 250 cc. of dry ether was added and the rest of a solution of 685 g. (5 moles) of the highly purified isobutyl bromide in 625 cc. of dry ether was added as follows. Half of the solution was added during seven and a half hours. Then the remaining half was diluted with 375 cc. of dry ether and added during six and a half hours. The temperature of the reaction mixture was at all times below 50°. The trapped material amounted to 46 g. (0.8 mole) and was mainly isobutane and isobutylene. Titration of an aliquot part of the clear Grignard solution with standard acid showed that 3.7 moles of butylmagnesium bromide had been formed.

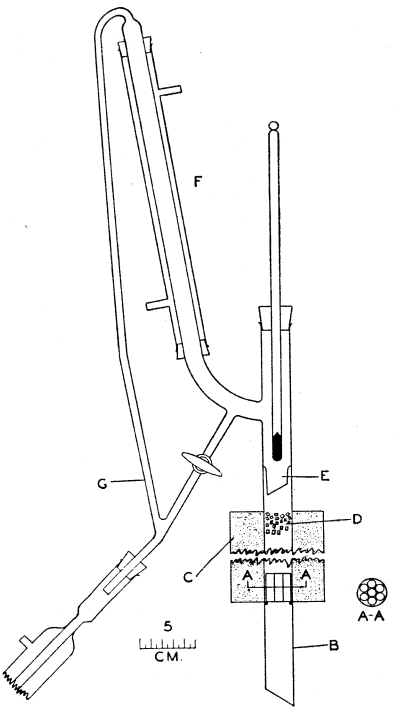


Fig. 1.—Several columns of this type were used in this study and in the researches described in the accompanying papers. A, A mat for holding up the packing in the column. It is made of several short pieces of glass tubing fused together, and rests on small indentations in the column. B, The column, of 20 mm. inside diameter Pyrex tubing measuring 100 cm. from the bottom to E, and about 115 cm. over-all. C, Magnesia pipe insulation. In some of the columns this was supplemented or replaced by electric heating coils (see Fig. 2). D, Packing made from 6-mm. glass tubing cut in 6-mm. lengths. This was kindly supplied by the du Pont Co. at cost. E, Drip indicator made by sealing a 15-mm. tube inside the column. F, Condenser made of 15-mm. Pyrex tubing with a jacket 25 cm. long. In some columns an internal condenser was used. In these, the drip indicator, E, was usually omitted as the reflux ratio could be calculated by counting the drops from the tip of the internal condenser instead of from E. G, Pyrex tubing 8 mm. in diameter with a stopcock having a 2-mm. bore. The take-off is adjusted by this stopcock. The tube G makes possible the use of the column under reduced pressure. Thus the ordinary disadvantages of distillations from Claisen flasks under reduced pressures are avoided.

Treatment of the Grignard Solution with Oxygen.—The solution was filtered through glass wool into a 5-liter flask equipped with a mercury-sealed stirrer, a thermometer, an inlet tube and an efficient reflux condenser attached to a mercury trap having a head of about 2.5 cm. of mercury.

The solution was diluted with 2250 cc. of ether, the inlet tube was adjusted to reach to about 2 cm. *above* the solution and stirring was started. After the solution had been cooled to −2° by an ice–salt mixture, dry oxygen was passed over the stirred cold solution at such a rate that none escaped through the mercury trap. The temperature was kept below 0° at all times. After about eight hours, the temperature dropped sharply and oxygen bubbled through the mercury trap. The treatment with oxygen at 0° or lower was continued for three hours.

The solution was added to a mixture of 1.5 kg. of cracked ice and 1.3 kg. of ammonium sulfate. The ether layer was separated and washed twice with 500-cc. portions of water which was added to the water layer. The water layer was extracted 10 times with 300-cc. portions of ether. The combined ether extracts were washed with water. The ether solutions were dried with 500 g. of anhydrous potassium carbonate. The ether was then removed by distillation through the 85 × 2 cm. column using a high reflux ratio. The residue was then carefully fractionated through a similar 38 × 1.8 cm. packed column as follows.

Fraction	Bar., mm.	B. p., °C.	Reflux ratio	Wt., g.
A1	742	60–67	15:1	0.7
2		67–81	8:1	2.5
3		85–90	60:1	13.0
4	745	90–95	60:1	17.0
5		95–100	60:1	2.0
6		100–106	60:1	2.5
7		106–107.2	60:1	7.0
8	742	107.2–107.4	60:1	78.5
9		107.4–107.8	60:1	90.5
10		107.8–107.9	60:1	21.0
11		Residue		8.5

Fractions A7–9 represent a 74% yield of isobutyl alcohol based on the Grignard reagent used. Fractions A2–4 were redistilled through a 55 × 0.8 cm. Vigreux column, bar. 743 mm.

Fraction	B. p., °C.	Reflux ratio	Wt., g.
	Starting with fractions A2, 3		
B1	60–79	2:1	0.5
2	79–85	2:1	1.0
3	85–89	5:1	
	Fraction A4 added		
	85.5–87	5:1	23.5
4	87–90	5:1	0.5
5	Residue		4.0

Fractions A5, 6, 7 and B2, 3, 4 were combined and distilled through a 90 × 1.2 cm. adiabatic column of the *partial* condensation type (Fig. 2), bar., 729–731 mm.

Fraction	B. p., °C.	Reflux ratio	Wt., g.	n_D^{20}
C1	84.6–85	46:1	0.5	
2	85–87	12:1	2.5	
3	87–89	20:1	12.0	1.4214

At this point it was found that the distillate contained halogen (Beilstein test and sodium ethylate test). The distillation was then completed in the small Vigreux column.

3a	90–96	2:1	2.5	1.4032
4	96–105	2:1	1.5	
5	105–106.2	20:1	7.5	

Fractions C3, 3a were redistilled through the Vigreux column. Bar., 734 mm.

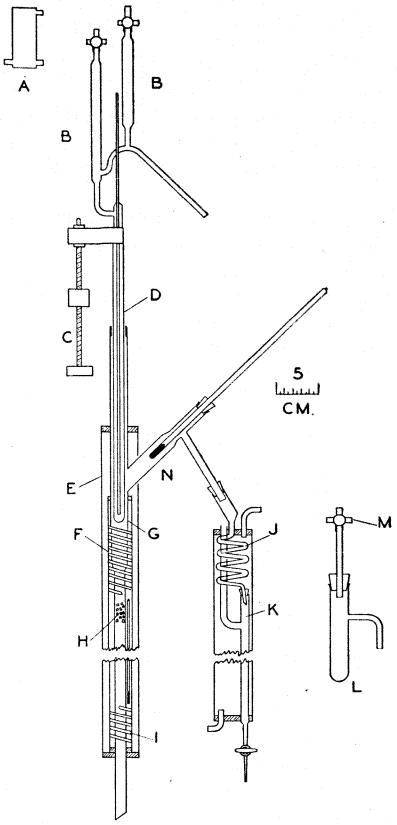


Fig. 2.—This column was designed by M. R. Fenske and constructed by Franklin Johnston for the separation of smaller amounts of liquids than those which can be separated by means of columns of the total condensation, partial take-off type (Fig. 1). A, A one-gallon can arranged to supply a constant head of water to the inside tube of the condenser D. The outlet of the condenser is connected to the drop indicator L and the flow of water through the condenser is regulated by the screw clamp M. B, Air traps to take air bubbles out of the line leading from the condenser to the drop indicator. If these traps are omitted, air bubbles prevent the accurate adjustment of the flow of condenser water which is necessary in careful separations. C, A brass screw 15 cm. long arranged to make possible the accurate raising and lowering of the condenser within the enlarged top of the column. D, Condenser 39 × 1 cm. The cooling water from the constant level device enters the middle tube of the condenser. The condenser can be raised or lowered inside the column by means of the screw C. At the start of a distillation, the condenser is lowered until no vapor passes through the side arm N. After the column has reached equilibrium, the condenser is raised to allow a slow stream of vapor to pass through N to the condenser J. If this stream of vapor is very slow, the readings of the thermometer are not significant. The course of the distillation is then followed by taking the refractive indices of the fractions. E, An insulating jacket consisting of a Pyrex tube 123 cm. long and 4.3 cm. inside diameter. F, A Pyrex tube, 115 cm. long and 2.7 cm. inside diameter, carrying the heating ribbon I. G, Column consisting of a Pyrex tube 29 cm. long and 2.1 cm. inside diameter sealed to the top of a Pyrex tube 113 × 1.2 cm. H, Packing consisting of Lessing rings, 5 × 5 mm., made of 50-mesh copper screen. Packed space, 90 cm. long. I, Heating ribbon. The jacket F is wrapped with 42 ft. (125 turns) of Chromel resistance ribbon, $^1/_{16}$ × 0.005 in., having a resistance of 1.68 ohms per ft.; total resistance, 70 ohms. A fixed outside resistance of 61 ohms and a variable resistance of 45 ohms with a capacity of 3.1 amp. are arranged to give the maximum flexibility in heating the column. The temperature of the column is given by a thermometer between the tubes F and G. J, A copper condenser consisting of 45 cm. of tubing 5 mm. outside diameter. K, A 10-cc. buret connected to the copper condenser. The buret and condenser are in a glass jacket through which cold water runs. L, Drop indicator connected to the outlet from the condenser D. This is used to measure the flow of cooling water through this condenser. M, Screw clamp used to regulate the flow of cooling water. By proper adjustment of the flow of water and the height of the condenser D in the column, the flow of vapor through N can be very accurately controlled. N, Side arm of column to convey the vapors which pass the partial condenser D to the total condenser J. The distance from the column to the second side arm is 9 cm.

D1	86.5–87	8:1	2.5	
2	87–89	8:1	7.0	1.4200
3	89–89.5	6:1	2.5	
4	Residue		1.0	

Analysis of Fraction D2.[9] Calcd. for C_4H_9Br: Br, 58.3. Found: Br, 45.3, 44.5; tertiary bromide, 0.3. No fraction corresponding to *tert.*-butyl alcohol was detected.

Separation of a Known Mixture Containing 98% Isobutyl Alcohol and 2% Tertiary Butyl Alcohol.—A mixture of 4 g. of *tert.*-butyl alcohol (m. p. 25°) and 196 g. of isobutyl alcohol (b. p. 107–108°) was fractionated through a 38 × 1.8 cm. packed column with total condenser and variable take-off.

Fraction	B. p., °C.	Reflux ratio	Wt., g.
E1	99.9–101	60:1	12
2	101–105.5	60:1	11.5
3	105.5–107	60:1	14
4	Residue		160

Fractions E1, 2, 3 were combined and fractionated through the 90 × 1.2 cm. partial condensation column (Fig. 2).

Fraction	B. p., °C.	Reflux ratio	Wt., g.
F1	78	26:1	1.3
2	81.2–85.8	26:1	1.5

Fraction F1 did not freeze at −10° but F2 had a m. p. of +6°. The two fractions were mixed with concentrated hydrochloric acid (16 cc.) and an oily layer separated. This was dried with potassium carbonate and then had the correct b. p. for tertiary butyl chloride, 50–50.5°.

Preparation of Tertiary Butyl Alcohol from Tertiary Butylmagnesium Chloride.—The Grignard reagent was prepared from one mole each of tertiary butyl chloride and magnesium in the usual way, yield 60%. The solution was diluted with more ether, making a total of 600 cc. of ether, and treated with oxygen below 0°. The mixture was poured on ice. The ether layer was distilled in the usual way, the alcohol fractions being distilled through the 38 × 1.4 cm. column.

Fraction	B. p., °C.	Reflux ratio	Wt., g.	M. p., °C.
G1	62–78	30:1	6	− 8
2	78–81.8	30:1	24	+ 8
3	Residue		4	+21

Summary

1. No rearrangement to tertiary butyl compounds is found when pure isobutyl bromide is converted to the Grignard compound and then to isobutyl alcohol by the action of oxygen.

2. The possible relation of these facts to the theoretical consideration of rearrangements and of the Grignard reaction is indicated.

STATE COLLEGE, PENNSYLVANIA

[9] *Cf.* Meisenheimer and Schlichenmaier, *Ber.*, **61**, 2029 (1928).

NOTE

The Oxidation of Optochin

By C. C. Vernon and H. U. Resch

Introduction.—Attempts have been made to reduce the toxicity of optochin[1] by altering the structure of its molecule,[2] since the drug has been shown to have certain desirable properties,[3] and has given promise of being a specific for pneumococci.[4] During such a study in this Laboratory it was necessary to prepare 6-ethoxyquinoline-carboxylic acid-4. In order that there might be no question as to structure, it was proposed to prepare this compound by direct oxidation of optochin. This should be a reliable method, because optochin (ethyl hydrocupreine) closely resembles quinine (methyl cupreine) in structure and chemical properties.[5] Skraup[6] has prepared quininic acid (6-methoxyquinoline-carboxylic acid-4) by the oxidation of quinine, in much the same fashion as described in this article.

Experimental

A solution containing 10 g. (0.029 mole) of optochin and 30 g. (0.328 mole) of sulfuric acid in 200 g. of water was heated to boiling in a flask fitted with a reflux condenser and dropping funnel. A cold saturated solution of chromic oxide in water, containing 20 g. (0.132 mole) in all, was slowly added to the boiling solution, over a period of ninety minutes. Boiling was continued for thirty to sixty minutes, and then sufficient ethyl alcohol was added to reduce the remaining oxidizing agent. The cooled reaction mixture was treated with a solution of 90 g. of potassium hydroxide dissolved in 500 cc. of water, and the gelatinous mass of chromium hydroxide filtered out. The filtrate was exactly neutralized with sulfuric acid, and concentrated to a volume of not more than 300 cc. An equal volume of 95% ethyl alcohol was added and the precipitated potassium sulfate removed by filtration. The alcohol was recovered from the filtrate by distillation and the remaining solution concentrated to approximately 50 cc. over a water-bath. Any precipitate appearing at this point was discarded, and 3 g. (7.1 cc. of a 36% solution) of hydrochloric acid added. After fifteen minutes' heating over a water-bath, yellow needles formed in this solution upon cooling to room temperature. Several crops of these crystals were secured by further concentration of this solution before the residue became so saturated with tarry materials that further treatment was useless.

---

[1] Oliver, *Brit. Med. J.*, **1**, 580 (1916); Kolmer and Idzumi, *J. Inf. Dis.*, **26**, 355–371(1920).

[2] Meyer and Gottlieb, "Experimental Pharmacology," Lippincott Company, Philadelphia, 1926, 7th ed., p. 557; Heffter, "Handbuch der experimentellen Pharmakologie," Julius Springer, Berlin, 1920, Vol. II, pt. 1, pp. 96–99.

[3] Woringer, *Arch. de Med. d. enf., Paris*, **27**, 713–725 (1924); Kolmer and Sands, *J. Exp. Med.*, **33**, 693–713 (1921); Morgenroth and Levy, *Berl. Wochenschr.*, **48**, 1561, 1650, 1779, 1983 (1911).

[4] Smith and Fantiss, *J. Pharm. Exptl. Ther.*, **8**, 53 (1916); Weiss, *J. Inf. Dis.*, **22**, 573 (1918).

[5] Heffter, "Handbuch der experimentellen Pharmakologie," Julius Springer, Berlin, 1920, Vol. II, pt. 1, p. 96.

[6] Skraup, *Ber.*, **12**, 1104 (1879).

The product so prepared melted at 231–233°. It was insoluble in ether, chloroform, ethyl acetate and benzene. It crystallized from hot 95% ethyl alcohol in beautiful lemon yellow needles having a final melting point of 288.5°.

Anal. Qualitative: C, H, N, +; S, Cl, −. Calcd. for $C_{12}H_{11}O_3N$: C, 66.35; H, 5.07. Found: C, 66.32; H, 5.00.

The yield of the product melting at 231–233°, as shown in three separate runs, averaged slightly below 20%. The yield of the product melting at 288.5° was approximately 12% of the theoretical. This low yield was believed to be due to the retention of much of the product in the precipitated chromium hydroxide, which was difficult to filter out, and almost impossible to wash.

Summary.—Optochin has been oxidized with chromic oxide in an acid solution. The analysis of the product, and its method of preparation, indicated that it was 6-ethoxyquinoline-carboxylic acid-4.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
SCHOOL OF MEDICINE
UNIVERSITY OF LOUISVILLE
LOUISVILLE, KENTUCKY

RECEIVED MAY 23, 1932
PUBLISHED AUGUST 5, 1932

COMMUNICATIONS TO THE EDITOR

THE POTENTIAL OF THE Ag(s), AgCl(s), KCl(aq), AgCl(s), Ag(s) CELL, SHOWING THE EFFECT OF FLOWING THE ELECTROLYTE OVER ONE ELECTRODE ONLY

Sir:

Carmody, in a recent note [THIS JOURNAL, **52,** 210 (1932)], states that when the electrloyte is flowing over a Ag(s), AgCl(s) electrode, there is a difference of 0.006 volt positive to a Ag(s), AgCl(s) electrode at equilibrium with the cell solution [p. 191]. This note was written because the value obtained for the Pb, Pb^{++} potential by Randall and Cann [THIS JOURNAL, **52,** 589 (1930)] was 0.1203 v. whereas Carmody [THIS JOURNAL **51,** 2905 (1929)] had obtained the value 0.1263 v. The difference in values was attributed by Carmody to the fact that Randall and Cann had allowed the electrolyte to flow over the Ag(s)–AgCl(s) electrode.

Because of this apparent discrepancy the authors investigated the cell Ag(s), AgCl(s), KCl(aq), AgCl(s), Ag(s), using an H-cell, set up according to Fig. 1, keeping the electrolyte on one side stationary, and allowing it on the other side to be in motion, entering the cell at I and leaving it at II. The Ag(s)–AgCl(s) electrodes were prepared in precisely the same way as had been done previously by Randall and Cann, care being taken to free them from adsorbed gas. The electrodes were white because they were protected from all light. Every operation was performed in containers painted black on the outside. Two cells were made, one containing 0.025 *M* KCl and the other 0.05 *M* KCl. All measurements were made with a Type K potentiometer, using an oil-bath regulated at 25°.

Analysis of the results reveals the following facts. First, readings were always taken with the electrolyte on both sides of the cell stationary. In each case a period of at least twenty-four hours was allowed for this equilibrium to be obtained. After the flow of the electrolyte was started, a period of about twenty minutes was allowed to elapse before any readings were taken, in order to permit the cell to come to equilibrium under the new conditions. When the electrolyte was flowing, the potentials were always negative to those obtained when the electrolyte was stationary.

More than forty readings were taken on Cell A and about fifteen on Cell B. With Cell A the readings varied from the lowest values of −0.00023 v. to the highest of −0.00162 v. With Cell B the lowest reading was −0.00072 v. and the highest −0.00190 v. The average of the differences from the mean in Cell A was 0.00038, and the average deviation of the average differences was 0.000078. The average of the differences from the mean in Cell B was 0.00031 and the average deviation of the average differences was 0.0001.

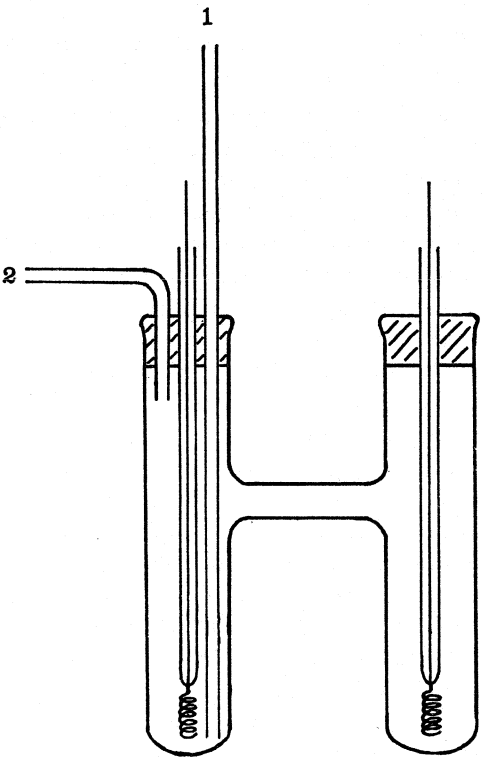


Fig. 1.

It might seem that the greater the rate of flow the more negative the difference becomes. A large variety of different rates of flow was examined, but apparently no definite relationship exists between rate of flow and difference of potential. Also, readings of the barometer were invariably taken, but the variations in this value, a maximum of eight millimeters, appeared to have no effect. The average difference in potential due to the flowing of the electrolyte in Cell A was −0.00074 v., and that in Cell B was −0.00100 v.

These results indicate that Carmody is correct in his contention that there is a drop of potential when electrolyte is flowing over the Ag(s), AgCl(s) electrode. But the value obtained by us, using potassium chloride as the electrolyte, is much less than that suggested by Carmody, who used hydrochloric acid as the electrolyte. Our values of −0.00074 and

−0.00100 are not sufficient to account for the discrepancy between the values of 0.1203 v. for the Pb, Pb^{++} electrode as obtained by Randall and Cann and the value of 0.1263 v. as obtained by Carmody.

DEPARTMENT OF CHEMISTRY
SMITH COLLEGE
NORTHAMPTON, MASSACHUSETTS
JESSIE Y. CANN
ELIZABETH LA RUE

RECEIVED JUNE 17, 1932
PUBLISHED AUGUST 5, 1932

THE CONSTITUTION OF BORNYL ANILINE

Sir:

In a recent publication, P. Lipp and G. Stutzinger [*Ber.*, **65**, 241 (1932)] presented evidence purporting to establish the identity of the so-called "bornyl aniline" of Ullmann and Schmidt [*ibid.*, **43**, 3202 (1910)] with the secondary amine obtained by the condensation of aniline with camphene in the presence of aniline hydrochloride and also with the amine resulting from the reduction of camphor anil with hydrogen and platinum. These findings have duplicated in part investigations well under way in this Laboratory, on which a preliminary report was presented by the authors at the recent Fall Meeting of the American Chemical Society at Buffalo, N. Y., under the title "The Fixation of Aniline by Hydrocarbons of the Terpene Series." The results of our experiments confirm the statement of L. and S. as to the identity of the camphene-aniline condensate with "bornyl aniline," but appear to be at variance with regard to the amine obtained from camphor anil by reduction. We performed the reduction of the anil with sodium and aniline as the reducing medium, obtaining a secondary amine whose acetyl derivative melted at 112–113° while L. and S. report 123° as the melting point of their product. The behavior of these amines, and also one obtained by the condensation of aniline with α-pinene in the presence of aniline hydrochloride are under investigation in this Laboratory in a further attempt to establish their structures by exhaustive methylation. The bornyl aniline of Ullmann and Schmidt and also that obtained from camphene have been found to yield camphene nearly quantatively, while those obtained from α-pinene and reduced camphor anil exhibit behavior on exhaustive methylation which is similar to that of bornyl amine.

We expect to publish a complete account of this investigation in the near future.

DEPARTMENT OF CHEMISTRY
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK, N. Y.
JOHN J. RITTER
HENRY O. MOTTERN

RECEIVED JUNE 18, 1932
PUBLISHED AUGUST 5, 1932

THE HEAT CAPACITY OF SOME HYDROGEN HALIDES AT HIGH TEMPERATURES AS CALCULATED FROM RAMAN SPECTRA

Sir:

The existing data on the heat capacity of the hydrogen halides in gaseous form are very meager and are on the whole unsatisfactory as Eastman [*Bur. Mines, Tech. Paper* 445 (1929)] has pointed out in his critical summary of the specific heats of gases. Experimental evidence on HBr, HI and HF is entirely lacking, while such data as are available for HCl leave something to be desired. Since the heat capacities of N_2 and HCl are practically identical in so far as one can tell from the fragmentary evidence on the latter, and since the energy of the lower levels in the molecules of HCl, HBr and HI is not very different from that of the corresponding level in N_2, Eastman assigned to the three halide gases the heat capacity of N_2, which is known with reasonable accuracy. This assumption, which admittedly introduces some error, was nevertheless the best one that could be made under the circumstances.

Since the methods heretofore employed in making heat capacity measurements at high temperatures have involved a difficult technique and have led in a great many cases to questionable results, it seems not unlikely that for a polar molecule calculations based on the well-known Planck–Einstein specific heat equation may in the end be more satisfactory than direct observations, in spite of the fact that such factors as the increases in potential energy due to stretching of the molecule are neglected.

Reliable values of the fundamental frequency of vibration of HCl, HBr and HI have recently been derived by Salant and Sandow [*Phys. Rev.*, **37**, 373 (1931)] from Raman spectra. Using their results (HCl, $\Delta^1/\lambda = 2886$ cm.$^{-1}$, HBr, $\Delta^1/\lambda = 2558$ cm.$^{-1}$, HI, $\Delta^1/\lambda = 2233$ cm.$^{-1}$) it is possible to calculate the heat capacity of these gases with an accuracy apparently somewhat greater than that of the values selected by Eastman, which are probably the best of the existing data.

Such a calculation has been made and the results, expressed as C_p ($C_p = C_v + R$), are shown in the accompanying table. The single set of

TABLE I

HEAT CAPACITY OF HYDROGEN HALIDES

Temp., °K.	C_p HCl as calcd.	C_p HBr calcd.	C_p HI calcd.	C_p Eastman's best value
600	7.07	7.13	7.26	7.17
800	7.28	7.44	7.58	7.33
1000	7.54	7.71	7.86	7.50
1200	7.78	7.94	8.10	7.67
1400	7.98	8.12	8.28	7.86
1600	8.14	8.28	8.42	8.06
1800	8.28	8.40	8.53	8.27
2000	8.38	8.48	8.59	8.49

values chosen by Eastman as representing the heat capacity of all three halide gases has been included for comparison.

It will be seen that the agreement between Eastman's selected figures and the calculated values for HCl is satisfactory, the maximum deviation being approximately 1.5%. It is perhaps worth noting that above 2000° Eastman's values run higher than the calculated ones and that this is the same direction in which Eastman's values deviate from the best of the experimental observations.

For HBr and HI differences as great as 5% exist between the results of the calculations and the data of Eastman. Unfortunately there appear to be no experimental observations on which to check the calculations but in view of the agreement found with HCl it seems probable that the calculated values are not much in error and almost certainly give a closer description of the true heat capacity of these gases than is obtained by assigning the same figure to all.

THE RESEARCH LABORATORY
UNITED STATES STEEL CORP.
KEARNY, N. J.

J. B. AUSTIN

RECEIVED JUNE 22, 1932
PUBLISHED AUGUST 5, 1932

THE CHLORINATION OF NEOPENTANE

Sir:

All recorded methods of making neopentane failed to give appreciable yields except that of Lwow [*Z. Chem.*, 520 (1870)] involving dimethyl zinc and a tertiary butyl halide. The iodide, bromide and chloride gave 42, 46 and 51% yields, respectively. The hydrocarbon froze and boiled at approximately −20 and +10°, respectively.

The chlorination of neopentane was very easy. At room temperature in diffused light the color of chlorine disappeared in fifteen minutes. The chloride boiled at 24° (80 mm.) and froze at −20°. The analysis for chlorine was 1.5% low for an amyl chloride. Tertiary amyl chloride showed b. p. 23.5° (8 mm.) and m. p. −73°. A small amount of a dihalide, b. p. 35° (8 mm.), was also obtained. The monochloride when shaken with cold water for thirty minutes showed the presence of 6% of tertiary halide (Michael). The amount of tertiary halide was increased only slightly, if at all, by heating the chloride at 140° for one and one-half hours. All known methods of converting a halide to a Grignard reagent failed. These facts indicate that the halide obtained is neopentyl chloride.

Neopentane is being prepared in larger amounts to make possible a more thorough study of its chlorination in relation to the mechanism of rearrangements. The limited amount of tertiary amyl chloride formed and the surprising stability of the neopentyl chloride carry implications of great

significance in this field [Whitmore, THIS JOURNAL, **54**, 3274 (1932); Whitmore and Rothrock, *ibid.*, **54**, 3431 (1932)].

DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

GEO. H. FLEMING
FRANK C. WHITMORE

RECEIVED JUNE 27, 1932
PUBLISHED AUGUST 5, 1932

DEHYDRATION OF DIETHYLCARBINOL

Sir:

By dehydrating diethylcarbinol in a flow reactor at 40 lb. pressure and at 365–410° with a phosphoric acid catalyst on silica gel we have obtained a mixture of olefins of b. p. 65–70° which on ozonolysis gives formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde. The first two were identified by the resorcinol–sulfuric acid test and as acetaldehyde–ammonia, respectively. The last two were converted to the 2,4-dinitrophenylhydrazones, which were identified by melting point and mixed melting point determinations. Small amounts of impure 2,4-dinitrophenylhydrazones probably corresponding to methyl ethyl ketone and diethyl ketone were also obtained. These results show that the dehydration of diethylcarbinol gives both the normal and rearranged products. This study is to be continued on a larger scale in an endeavor to determine quantitatively the various modes of dehydration.

DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

F. A. KARNATZ
FRANK C. WHITMORE

RECEIVED JUNE 27, 1932
PUBLISHED AUGUST 5, 1932

THE REACTION OF ACID IODIDES WITH ETHERS

Sir:

In a recent paper by Meerwein and Maier-Hüser [*J. prakt. Chem.*, **134**, 51 (1932)] on the cleavage of ethers by acid halides and anhydrides in the presence of catalysts, these workers have called attention to the isolated observation of Kishner [*J. Russ. Phys.-Chem. Soc.*, **41**, 651–659 (1909); *Chem. Zentr.*, II, 1132 (1909)] that benzoyl iodide is capable of splitting primary aliphatic ethers at 100° without the presence of a catalyst, giving alkyl iodides and benzoates. This work has not previously received the further study which its suggestive character would indicate.

With the hope that aliphatic acid iodides might prove more reactive, permitting the cleavage of ethers at ordinary temperatures, we have investigated the behavior of acetyl iodide and the chloro substituted acetyl iodides with a number of aliphatic ethers, thio ethers and oxides. This

study has shown that the cleavage reaction between acid iodides and ethers proceeds in all probability through a preliminary formation of an oxonium compound between the ether and the acid iodide.

Secondary ethers have been found to be much more readily cleaved into alkyl iodides and esters than are primary ethers. The substitution of chlorine in the α-position in aliphatic acid iodides has been found to diminish their ability to cleave ethers. The tendency of acetyl iodide, chloroacetyl iodide and dichloroacetyl iodide to split primary ethers was found to be diminished by increasing substitution of chlorine. Trichloroacetyl iodide showed no tendency to cleave either primary or secondary ethers at ordinary temperatures even in the presence of zinc iodide as a catalyst, though evidence of the formation of an oxonium compound was obtained. Similarly, substitution of chlorine in the α-position in aliphatic ethers greatly increased their resistance to cleavage by acid iodides.

SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

EDWIN L. GUSTUS
PHILIP G. STEVENS

RECEIVED JULY 11, 1932
PUBLISHED AUGUST 5, 1932

IS THE NUTRILITE FOR "GEBRÜDE MAYER" YEAST OF UNIVERSAL BIOLOGICAL IMPORTANCE?

Sir:

We have obtained a considerable body of evidence that a single unknown hydroxy acid with molecular weight about 200 is the responsible agent for a remarkable growth stimulation of "Gebrüde Mayer" yeast.[1] Furthermore, what appears to be this same acid has been found universally in a great variety of living tissues.

The tissues extracted include (1) rice polish (Spermatophyta), (2) Aspergillus niger (Fungi), (3) Spirogyra and Oscillatoria, mixed (Algae), (4) Bacillus subtilis (Schizophyta), (5) Planarian worms (Plathylminthes), (6) Earthworms (Annulata), (7) Oysters (Mollusca), (8) Sea urchin eggs (Echinodermata), (9) Crabs eggs (Arthropoda), (10) Beef liver (Chordata), (11) Milk (Chordata). Not only was a growth stimulating substance present in every extract but on fractional electrolysis in an eight-compartment cell the activity in each case migrated under our experimental conditions to a cell with P_H value of about 4 and was usually completely removed from cells having a P_H of 5 or more.

[1] The criticism of Richards [*J. Biol. Chem.*, **96**, 416 (1932)] that our results may have been due to inorganic materials is not valid inasmuch as the article cited [THIS JOURNAL, **53**, 4171 (1931)] states that the activity was lost on ignition (p. 4176). Yeast nutrition like mammalian nutrition is undoubtedly affected by traces of elements of less frequent occurrence, but the effect of unknown organic materials is of entirely different order of magnitude and operates over an incomparably larger range.

The diffusion constant of the active substance (using rice polish and beef liver as sources) indicates that its molecular weight is about 200. The acid (rice polish was the source) has no primary or secondary amino group (nitrous acid anhydride treatment). It has been esterified with both methyl and ethyl alcohols. The esters are not basic (fractional electrolysis), hence the acid is not amphoteric. The presence of several hydroxy groups is indicated by (1) complete destruction of the active substance by treatment with dimethyl sulfate in the cold, (2) complete nonvolatility of the methyl ester at a pressure of 10^{-3} mm., (3) solubility of the esters in water and comparatively slight solubility in ether. The activity is not destroyed by hydrogenation following the methods of Roger Adams *et al.*, indicating that the substance is not olefinic and contains no aldehyde nor ketone group nor aromatic nucleus.

The possibility of the universal occurrence of a single acid substance of the character we have indicated opens up some very interesting questions. There is fragmentary evidence that the same acid may function in the growth stimulation of certain bacteria, molds and mushrooms and that it is one of the substances involved in the growth stimulation of other yeasts such as Wildiers' and No. 578 (American Type Culture Collection). The presence of this acidic substance in soils and composts suggests the possibility that it may function in the stimulation of the growth of green plants. It is synthesized by the mold Aspergillus niger, and seems to be more widely and evenly distributed in tissues than any known vitamin.

Because of their rather far reaching interest we wish at present to emphasize the tentative character of our conclusions [THIS JOURNAL, **53**, 4171 (1931)].

CHEMICAL LABORATORY
UNIVERSITY OF OREGON
EUGENE, OREGON

ROGER J. WILLIAMS
CARL M. LYMAN
GEORGE H. GOODYEAR
JOHN H. TRUESDAIL

RECEIVED JULY 1, 1932
PUBLISHED AUGUST 5, 1932

NEW BOOKS

Quantitative Chemical Analysis. An Intermediate Textbook. By FRANK CLOWES and J. BERNARD COLEMAN. Revised by D. STOCKDALE and J. DEXTER. Thirteenth edition. P. Blakiston's Son and Co., Inc., 1012 Walnut St., Philadelphia, Pa., 1931. xiv + 605 pp. Illustrated. 14.5 × 23 cm.

Analytical Factors and their Logarithms. By EARLE RADCLIFFE CALEY, M.Sc., Ph.D., Assistant Professor of Chemistry in Princeton University. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. v + 112 pp. 13 × 20 cm. Price, $2.00.

The first of these volumes, originally published forty-one years ago as a laboratory textbook, is now a rather complete manual on the art of quantitative analysis. The book is divided into eight parts: (I) (65 pages) general processes; (II) (58 pages) simple gravimetric estimations; (III)

(93 pages) volumetric analysis; (IV) (38 pages) miscellaneous methods of analysis; (V) (216 pages) general quantitative analysis; (VI) (32 pages) organic analysis and determination of molecular weights; (VII) (43 pages) gas analysis; (VIII) (60 pages) tables of reference and a table of four place logarithms.

Despite its size the book is designed primarily for student use. Not only are the directions for carrying out the various analyses admirably clear and complete but the arrangement of the experiments is, in general, one of progressive complexity and difficulty. Parts I–III cover the ground of the elementary first course in quantitative analysis as it is usually given in this country. However, instead of the few typical experiments there is described a variety of experiments of the same type. Thus, for example, in Part II directions are given for about forty simple gravimetric determinations. Part IV contains descriptions of electrolytic determinations, electrometric measurements with the hydrogen electrode and by oxidation–reduction methods, colorimetric measurements, and a bare mention of spectrum and x-ray analysis. The remainder of the book—slightly more than half—is devoted to standard methods of analysis which are essentially technical in character. To illustrate the nature of this section, some of the material included in Part V may be mentioned: analysis of ores and coal, water analysis, food analysis, and the estimation of oils and fats.

The broad scope and viewpoint of the book together make it particularly well suited to the requirements of the advanced student or graduate who has frequent occasion to refer to standard methods of analysis with which he is not familiar. For this purpose especially the book can be highly recommended.

The second of the volumes listed above is a collection of tables planned to meet the needs of the analytical chemist. The tables of gravimetric factors which occupy the first two-thirds of the book comprise factors for metallo-organic as well as inorganic precipitates, and also, briefly, factors necessary for the more common indirect weighings, indirect analyses, and weight conversions. A serviceable feature of these tables is the inclusion of the correct temperatures for the drying or ignition of the various precipitates. Furthermore, for most of the metallo-organic precipitates reference is given to leading papers bearing on their use. The last third of the book is given over to tables of volumetric factors, a "convenient generic term" which is employed to denote, "in general, the grams of substance present in a cubic centimeter of normal solutions of the elements or compounds listed." These factors include those elements and substances which can be determined by standard methods of volumetric analysis. At the end of the book is a table of five place logarithms and a series of explanatory notes indicating the use and possibilities of the different tables.

The tables are quite comprehensive and are very conveniently arranged. The book, as the reviewer already has had the opportunity to discover, will be practically valuable as a time saver in the analytical laboratory.

ARTHUR F. SCOTT

Microchemical Laboratory Manual. By FRIEDRICH EMICH. With a Section on Spot Analysis by Dr. FRITZ FEIGL. Translated by FRANK SCHNEIDER, Sc.M. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1932. xvi + 180 pp. 88 figs. 15.5 × 23.5 cm. Price, $2.75.

The appearance of Emich's admirable little text in English will meet with a ready welcome. This book is intended as an introduction to microchemical practice and presents sufficient material for a course of one semester. While many will not agree with the translator's prefatory statement regarding "the lack of an adequate text on the subject in English" in view of Chamot and Mason's excellent manual (to which Emich repeatedly refers in the text), there is ample room in this rapidly growing field for fresh points of view. The translation has an easy, readable style and the translator deserves credit for making the book available in English.

LAWRENCE T. FAIRHALL

Colloids. By ERNEST S. HEDGES, M.Sc., Ph.D. (Manchester), D.Sc.(London), A. I. C. Longmans, Green and Co., 55 Fifth Ave., New York, 1931. vii + 272 pp. Illustrated. 14 × 22 cm. Price, $4.50.

Hedges has produced a fresh and distinctive treatment of the subject of Colloids which takes its place with the other introductions to that important field. The book is based to a large extent upon recent papers which have attracted the author's interest, although there is a refreshing number of references to important papers in the older literature. It is remarkable for its studious avoidance of quantitative formulations. The attempt is made rather to give a vivid mental image of the structure and behavior of colloidal systems, an object which is eminently desirable. Indeed if pushed still further it would help in the logical discrimination between confused or conflicting conceptions. In other words, the development of colloid science would benefit greatly from the setting up of models as working hypotheses and there is a much greater probability of such models possessing permanent validity than those used in the elucidation of atomic structure.

If the author had only pursued this method more consistently he would not have stated (p. 5) that "colloidal gold is a physical system composed of water and of gold in a certain state of subdivision," when from certain later pages it is evident that the author is aware that there is likewise an essential, partly dissociated, stabilizing agent present. The author has rightfully emphasized the properties of gels "because natural colloids

appear more often in the form of gels than sols." His description faithfully reflects the muddled state of the subject, which may be summarized in his opening sentence on the structure of gels (p. 207), "There is still considerable divergence of opinion about the structure of gels, but several of the accepted views approximate closely to the same thing when studied seriously."

The book is attractive, with good print and diagrams. Although many statements are debatable, Hedges' introductory presentation may be warmly recommended as being modern, stimulating, and original in its selection of subject matter.

JAMES W. MCBAIN

Annual Review of Biochemistry. Volume I. Edited by JAMES MURRAY LUCK, Stanford University. Stanford University Press, Stanford University, California, 1932. vii + 724 pp. 15.5 × 23 cm. Price, $5.00.

The extremely rapid development of most of the sciences since the beginning of the century has brought along with it an enormous increase in the periodical literature pertaining thereto. This is conspicuously true of the so-called "borderline" sciences, like biochemistry, that present overlapping fields of interest to their devotees. The day has long since passed when even the most assiduous student could be expected to become familiar at first hand with the thousands of pages contributed each year to the scientific journals concerned with research in his department of knowledge. The development of abstract journals and reviews has thus become both inevitable and highly essential.

The newly launched enterprise, *The Annual Review of Biochemistry*, sponsored so vigorously by Professor J. M. Luck and his colleagues: C. L. Alsberg, D. R. Hoagland and C. L. A. Schmidt, on the Pacific coast, is not entirely a novelty in its conception. It surpasses most of the other review journals or books in breadth of scope and in the noteworthy success with which so many collaborators of unusual competence have been secured. The new volume gives evidence of the never-to-be-forgotten fact that science transcends the boundaries of nations. Thus there are critical essays by R. Wurmser of France; I. Smedley-MacLean, L. J. Harris, E. G. Holmes, J. Needham and M. Stephenson, of England; R. Hoeber, A. Windaus and H. Fischer of Germany; J. K. Parnas of Poland; E. Waldschmidt-Leitz of Czechoslovakia; N. N. Ivanoff of Russia; H. D. Kay and J. B. Collip of Canada; P. Karrer and L. Ruzicka of Switzerland; in addition to fourteen reviews by American experts. This truly represents an international endeavor.

It would be futile to attempt any really critical comments in the confines of this necessarily brief notice of these very useful—and for the most part readable—seven hundred pages. To single out individual essays for special

mention seems presumptuous when so many masters of research have summarized the recent development in the domains of their own endeavors. A few themes have been treated somewhat scantily; but subsequent volumes are promised to remedy such temporary omissions. One can imagine the surprise awakened in some of the early contributors to another pioneer effort in reviewing the literature of physiological chemistry—Maly's *Jahresbericht ueber die Fortschritte der Thierchemie*—if they were to study this latest volume portraying the current state of the science. There would be vitamins and hormones and immunochemistry to perplex those older chemists by the utter novelty of the topics. The chemistry of muscle would give new meanings to old observations. The animal and plant pigments would present surprises of a new order. The physical chemistry of protoplasm would reveal old facts in new interpretations. *Tempora mutantur!*

LAFAYETTE B. MENDEL

BOOKS RECEIVED

June 15, 1932–July 15, 1932

FRITZ ARNDT. "Kurzes chemisches Praktikum für Mediziner und Landwirte." 14–17th edition. Verlag Walter de Gruyter, Genthiner Strasse 38, Berlin W 10, Germany. 100 pp. RM. 4.

MARCEL BOLL. "L'Idée Générale de la Mécanique Ondulatoire et de ses Premières Applications." Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. 74 pp. Fr. 15.

MARCEL BOLL. "Exposé Électronique des Lois de l'Électricité." Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. 72 pp. Fr. 15.

LOUIS DE BROGLIE. "Relations d'Incertitude." Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. 24 pp. Fr. 6.

LOUIS DE BROGLIE. "Théorie de la Quantification dans la Nouvelle Mécanique." Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. 250 pp. Fr. 70.

IRENE CURIE AND F. JOLIOT. "L'Existence du Neutron." Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. 22 pp. Fr. 6.

HARRY A. CURTIS, Editor. "Fixed Nitrogen." American Chemical Society Monograph. The Chemical Catalog Co., Inc., 419 Fourth Ave., New York. 517 pp. $12.00.

VICTOR FISCHL AND HANS SCHLOSSBERGER. "Handbuch der Chemotherapie." Part 1. Metal-Free Organic Compounds. Fischers Medizinische Buchhandlung, Antonstrasse 15/19, Leipzig C 1, Germany. 357 pp. M. 34; subscription, M. 29.

ADOLF JOLLES. "Die Vitamine nebst einer Einleitung über chemische Dynamik biologischer Vorgänge." Verlagsbuchhandlung Franz Deuticke, Wien, Austria. 157 pp. M. 10.

JOHN P. PETERS AND DONALD D. VAN SLYKE. "Quantitative Clinical Chemistry." Volume II, Methods. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Md. 957 pp. $10.00.

LEON B. RICHARDSON AND A. J. SCARLETT. "A Laboratory Manual of General Chemistry (Larger Edition Revised)." Henry Holt and Co., One Park Ave., New York. 143 pp. $1.50.

CESARE SERONO AND ALFONSO CRUTO. "Manuale di Analisi Chimica. Clinica, Fisio-Patologica ed Igienica ad Uso dei Medici e Studenti." Second edition. Unione Tipografico—Editrice Torinese, Torino, Italy. 483 pp.

HENRY C. SHERMAN. "Chemistry of Food and Nutrition." Fourth edition, revised and enlarged. The Macmillan Company, 60 Fifth Ave., New York. 614 pp. $3.00.

HERMANN STAUDINGER. "Die hochmolekularen organischen Verbindungen. Kautschuk und Cellulose." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 540 pp. RM. 49.60; bound, RM. 52.

VLASSIOS VLASSOPOULOS. "Neue Wege zur Erklärung des Wirkungsmechanismus der Fermente." Buchhandlung Gustav Fock G. m. b. H., Leipzig C 1, Germany. 70 pp.

"Bulletin of the Academy of Sciences of the United Provinces of Agra and Oudh, Allahabad, India." Published by the Council of the Academy of Sciences, Allahabad, India. 150 pp. + proceedings.

"Gmelins Handbuch der anorganischen Chemie." 8 Auflage. System-Nummer 59: Eisen. Teil B, Lieferung 5. Herausgegeben von der Deutschen Chemischen Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 394 pp. Mk. 53.50; subscribers, Mk. 47.

"Gmelins Handbuch der anorganischen Chemie." 8 Auflage. System-Nummer 58: Kobalt. Teil A, Lieferung 2. Herausgegeben von der Deutschen Chemischen Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 282 pp. Mk. 48; subscribers, Mk. 42.

"Memoires de la Chambre Centrale des Poids et Mesures de l'U. R. S. S. Présentés au Comité Consultatif d'Électricité et de Photométrie." Publication de l'Institut de Métrologie et Standardisation de l'U. R. S. S., Mejdounarodny 19, Leningrad, U. S. S. R. 147 pp. R. 3.00.